Effect of Hydrogen Sulfide, Ammonia and Water on Catalytic Hydrogenation of Propylbenzene

by

Syed Ahmed Ali

A Thesis Presented to the

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In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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University of Petroleum and Minerals

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under the direction of his Thesis Committee, and approved by all its members, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of

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Dedicated to

MY PARENTS

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خلاصـــــــــــــة

لقد تم بناء واختبار مفاعل يتحمل ضغوطا عاليه وذلك لدراسة التفاعلات التي تستخدم فيها الحفازات . ولقد تم دراسة التأثيرات الفرديه والجماعيه للكبريتيد الهيدروجين والنشادر والماء على هدرجه البروبايل بنزين في الحاله السائله ومع وجود حفاز . وجميع التجارب كانت عند درجـــات الحراره ٣٣٠ أو ٣٥٠ أو ٣٧٥ درجه مئويه كان ضغط الهيدروجين ١٠٠٠ باوند على البوصه المربعـــه ولقد استعمل الحفاز وهو النيكل والموليبدنيوم المحمول على الالومنيا في حالته الاكسيديه أو بعـــد كبرتته في المعمل . ولقد كان الضغط الجزئي لكبريتيد الهيدروجين والنشادر والماء هو ١٠٠ ملليمتـر زئبق لكل واحد منها (عندما تكون موجوده في المفاعل) . وحوالي واحد بالمائه من البروبايـــل بنزين في الهيكساديكين . ولقد تم تحليل العينات السائله بواسطة جهاز التحليل اللوني .

ولقد كان الناتج الوحيد لهدرجة البروبايل بنزين هو البروبايل سيكوهيكسين ولقد لوحـــظ أن هدرجة البروبايل بنزين على الحفاز المؤكسد أو المكبرت تتبع نظاما قانونا من الدرجه الاولـــى في تركيز البروبايل بنزين تحت جميع الظروف ولقد أثبتت النتائج أن وجود كبريتيد الهيدروجيـــن يقلل من معدل الهدرجه بحوالي ١٠ الى ٠/٠١٥ ويرجع هذا الى ملئ فراغات الكبريت السالبه على سطح الحفاز . أما وجود كبريتيد الهيدروجين والنشادر مع قلل من معدل الهدرجه بحوالـــــــي ٤٤ر٧ بالمائه عند ٣٣٠ درجه مئويه وحوالي ٤٢ر٨ بالمائه عند ٣٥٠ درجه مئويه وحوالي ٣٦ر٤ بالمائه عند ٣٧٥ درجه مئويه . وهذه الزيادة في خفض معدل الهدرجه يرجع الى الامتصاص الاقوى لنشـــادر ذو الخاصيه القاعديه العاليه على الاماكن الحمضيه على سطح الحفاز .

واضافة الماء وكبريتيد الهيدروجين مع النشادر لم يؤثر على معدل الهدرجه ومقارنـــــة أداء الحفاز المؤكسد بالحفاز المكبرت أثبتت أن قدرة الحفاز على الهدرجه زادت ٢٠ الـــــى ٢٥ ضعفا نتيجة الكبرته . ولقد وجد أن جميع الطاقات اللازمه لاتمام التفاعل تبلغ حوالي ١٧ الى ٢١ كيلو كالورى للمول الواحد .

ABSTRACT

A high-pressure reactor system for studying catalytic hydroprocessing reactions was constructed and tested. The autoclave was used as a liquid-phase batch slurry reactor for investigating the individual and simultaneous effects of hydrogen sulfide, ammonia and water on the kinetics of catalytic hydrogenation of propylbenzene. Experiments were carried out at 330, 350 and 375 °C under a hydrogen pressure of 1000 psig. with $NiMo/Al_2O_3$ commercial hydrotreating catalyst. The catalyst was used either in oxide form or after presulfiding it in the laboratory. The partial pressures of hydrogen sulfide, ammonia and water was kept at about 100 mm Hg. each (for the experiments in which their presence was needed). About 1 wt% of propylbenzene was taken in n-hexadecane. Liquid samples were analysed by Gas Chromatography.

Propylcyclohexane was the only product of propylbenzene hydrogenation. The hydrogenation of propylbenzene over both oxide and sulfided catalysts was observed to follow pseudo-first order kinetics in propylbenzene under all conditions studied. Results showed that due to the presence of hydrogen sulfide, the hydrogenation rate was reduced by 10-15 %. Filling of sulfur-anion vacancies is postulated as the cause for this effect. In the presence

of hydrogen sulfide and ammonia, the rate was inhibited by 44.7% at 330 °C, 42.8% at 350 °C and 36.4% at 375 °C. This increase in inhibition is due to the competitive adsorption of highly basic ammonia on the acidic sites. Addition of water to hydrogen sulfide and ammonia does not influence the rate of hydrogenation. Comparision of oxide and sulfided forms of $NiMo/Al_2O_3$ catalyst showed that the hydrogenation activity enhances by 20-25 times due to sulfiding. All apparent activation energies were found to be in the range of 17-21 kcal/gmol.

Chapter I

INTRODUCTION

1.1 Background:

The tremendous increase in world's energy consumption is evident by the rapid growth of crude oil production --- from the first well drilled in 1859 to the world's production of over 22 billion barrels in 1983. Over these years, the production and processing techniques of petroleum were highly developed. The liquid fuels thus derived are vastly being utilized for transportation, power generation and domestic uses. Petroleum products are also major feedstocks for the chemical industry. At the same time, the rate of discovery of new petroleum reserves does not keep pace with the increasing demand. Consequently, the efficient use of available resources and the search of alternative sources for the future generations have become two of the foremost objectives of the scientists and engineers throughout the world.

Petroleum residua and nonconventional fossil-fuel-derived materials are potentially significant alternative sources of energy and feedstock for chemical industry. Recently, there has been an upsurge in the development of production techniques and processing of synthetic crudes

derived from coal, oil shale and tar sands. The total recoverable reserves of these sources are much larger than crude oil and natural gas reserves (Matar, 1982). But synthetic crudes and petroleum residua are chemically more complex and less clean. One of the charecterstics is the higher concentrations of sulfur-, nitrogen- and oxygen-containing compounds (Qader et al., 1969; Snyder, 1970). Other features include higher concentrations of metals, such as vanadium and nickel; and lower H/C ratio, owing to the presence of significant quantities of polynuclear aromatics. Such a composition renders them unacceptable for direct processing in existing refineries and necessitates prior upgrading.

Table 1.1.1 illustrates typical sulfur, nitrogen and oxygen contents of representative light petroleum crude, petroleum residua and synthetic crudes. Since sulfur is the dominating heteroatom in petroleum feed stocks, catalytic hydrodesulfurization has been an important commercial process for quite some time. In addition to sulfur, coal derived liquids have much more oxygen while the nitrogen content in shale oil is as much as ten times of that present in most crude petroleum refined today.

Burning of fuels containing sulfur and nitrogen produces SO_2 and NO_x, both of which are severe atmospheric

Table 1.1.1

Elemental Analysis of Petroleum and Synthetic Crudes

wt%	Conventional Crude Oil	Safaniya Atm. Resid	Puraho Shale Oil	H-Coal Bituminous	Athabasca Bitumen
Carbon	86.00	84.92	84.30	89.00	83.36
Hydrogen	12.75	11.14	11.29	7.94	10.52
Sulfur	1.50	3.61	0.66	0.42	4.48
Nitrogen	0.20	0.24	2.18	0.77	0.43
Oxygen	0.05	0.09	1.16	1.87	0.62

Sources:
a) Gorbaty and Harney, 1979
b) Riley, 1978

pollutants. SO_2 has been the major concern with petroleum, but because of increasing restrictions on NO_x emission and the several-fold higher concentration of organo-nitrogen compounds in petroleum residua and synthetic crudes, nitrogen removal will become increasingly more important. Moreover, some heterocyclic nitrogen compounds may be quite carcinogenic.

Sulfur is a well-known poison for most of the metal-containing catalysts which are used in catalytic reforming, isomerization, hydrocracking etc. Catalytic reforming process utilizing platinum monometallic catalysts require feedstocks containing not more than 100 ppm sulfur. The $Rh\text{-}Pt/Al_2O_3$ catalysts are more sensitive to sulfur, and a level not exceeding the order of 1 ppm in the feedstock is typically required. Nitrogen compounds acts as poison for acid-catalysts, such as those used in catalytic cracking, hydrocracking and isomerization processes. Catalytic cracking can tolerate feedstocks having only a few hundred ppm of nitrogen (Satterfield, 1980).

So far, oxygen removal has not been studied carefully, partly because it is not a significant component in petroleum. It is not clear whether the removal of oxygen species is required in order to achieve desired product specifications. Certain oxygen-containing compounds are

acidic, and their presence, especially in commercial products, is unwelcome. In any event, if oxygen species are present, they may react. This can cause additional hydrogen consumption and may complicate nitrogen removal.

In short, to meet the specifications of commercial fuels, the removal of sulfur and nitrogen, prior to catalytic processing is essential.

1.2 Catalytic Hydroprocessing:

Industrially, the removal of sulfur and nitrogen is accomplished by catalytic hydroprocessing (also called hydrotreating). This is a pretreatment step wherein synthetic feedstocks are reacted with hydrogen in the presence of presulfided $NiMo/Al_2O_3$ or $CoMo/Al_2O_3$ catalyst, to yield commercially valuable liquid products.

Commercially, hydroprocessing is carried out in two types of reactors: trickle-bed reactors, in which liquid feed and hydrogen gas flow concurrently down through a stationary bed of catalyst; and slurry or ebullating-bed reactors, in which the catalyst is fluidized in a flow of gas and liquid. Hydrogen is separated from the product stream and recycled. Typical operating conditions for different classes of feedstocks are given in Table 1.2.1. It is obvious from the table that high pressures and

Table 1.2.1

Approximate Processing Conditions in Catalytic Hydroprocessing

Processing Conditions	Feedstock			
	Light Petroleum (distillates)	Heavy Petroleum (residua)	Coal Liquids	Shale Oils
Temperature, °C	300-400	340-425	400-460	375-475
Pressure, atm	35-70	54-170	135-270	150-300
LHSV, vol. feed/ vol.cat.hr	2-10	0.2-1	0.3-3.0	0.5-1
H_2 recycle, scf/bbl	300-2000	2000-10,000	>25,000	3000-10,000
Catalyst life, yrs	10	0.5-1	Undetermined	Undetermined

Sources: a) Katzer and Sivasubramanian, 1979.
b) Gates et al., 1979.

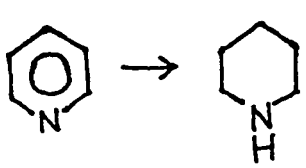
temperatures are required and that the severity increases as the feed changes from light petroleum to heavy petroleum to synthetic crudes.

During such a hydrotreating process, removal of sulfur, nitrogen and and oxygen occur. This is usually accompanied by hydrogenation of unsaturated hydrocarbons. Hydrocracking of long-chain aliphatics and of naphthenes also occur. The basic hydroprocessing reactions, alongwith specific examples, are as follows:

(1) Hydrodesulfurization (HDS); reactions leading to removal of sulfur from organic compounds by their conversion into hydrogen sulfide and hydrocarbons.

$$\rightarrow \quad CH_2 = CH - CH = CH_2 + H_2S$$

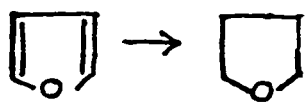
(2) Hydrodenitrogenation (HDN); conversion of nitrogen-containing organic compounds into ammonia and hydrocarbons.



$$\rightarrow \quad C_5H_{11}NH_2 \rightarrow \quad C_5H_{12} + NH_3$$

(3) Hydrodeoxygenation (HDO); removal of oxygen from

oxygen-containing organic compounds by their conversion into water and hydrocarbons.



$$\rightarrow C_4H_9OH \rightarrow C_4H_{10} + H_2O$$

(4) Hydrogenation of Aromatics; aromatic hydrocarbons get saturated to naphthenes. Polycyclic aromatics or large condensed ring structures are hydrocracked to give one- or two-ring aromatics. These are further hydrogenated to hydroaromatics or naphthenes consuming more hydrogen.

(5) Hydrocracking; hydrogenolysis of hydrocarbons to give refined fuels with smaller molecules and high H/C ratio.

$$R - CH_2 - CH_2 - R' \longrightarrow R - CH_3 + R' - CH_3$$

(6) Hydrodemetallation (HDM); removal of heavy metals, such as nickel and vanadium. These metals tend to

accumulate on catalysts during processing, decreasing catalyst effectiveness, and leading ultimately to irreversible deactivation.

The relative order of reactivity is

HDS > HDO > HDN > Hydrogenation of Aromatics

Hydrotreating catalysts consists of a primary metal component such as molybdenum or tungsten, promoted by nickel or cobalt and supported on γ-Al_2O_3. These catalysts are dual-functional; in that they possess both hydrogenation-dehydrogenation as well as hydrogenolysis activity. Any of these catalysts can catalyze all hydroprocessing reactions, but the selectivity is different for each catalyst.

1.3 Scope of Investigations:

One approach to an understanding of the catalytic chemistry and reaction kinetics of such processes is to study the reactivity of representative compounds that are present in the actual feedstocks. Recent studies (Goudriaan, 1974; Shih et al., 1977; Gultekin, 1980; Gultekin et al., 1984) are revealing the nature of interactions that may occur between the princpal classes of compounds present, both as reactants and products, and

thereby provide guidance for the improvement of commercial processing.

The HDN of heterocyclic nitrogen compounds occur via a complex reaction network involving saturation of heterocyclic rings followed by carbon-nitrogen bond scission (McIlvried, 1971). In contrast to HDN, HDS involves largely direct extrusion of sulfur from thiophenic ring (Desikan and Amberg, 1964). With oxygen compounds, it was found that the saturation of aromatic rings is a prerequisite for carbon-oxygen bond scission, analogous to HDN (Rollmann, 1977). Thus, in order to achieve reasonable HDN and HDO, conditions should be viable for hydrogenation of aromatic rings.

Feedstocks usually contain considerable fractions of aromatic hydrocarbons. It can be surmised that they may also hydrogenate under the reaction conditions. But the hydrogenation of monocyclic aromatic hydrocarbons is not desirable for two major reasons:

(1) It will decrease octane number. For a product to be blended into gasoline, it is desirable to minimize the hydrogenation of mono-olefins and of aromatics in order not to reduce the octane number of the gasoline.

(2) It will consume costly hydrogen. Hydrogen is expensive to manufacture, so it is desirable to

operate all hydrotreating processes to optimize the desired reactions and yet minimize the hydrogen consumption.

Hence reaction conditions must be selected very carefully in order to assure that optimum level of aromatic saturation occurs. The literature on aromatic hydrogenation in the presence of a commercial hydrotreating catalyst is sparse and provides almost no interpretation demonstrating the effects of important process variables. Information regarding the interaction between other reactions and hydrogenation of aromatic hydrocarbons is also sorely lacking. But due to the important reasons mentioned above, there is a need for better understanding of the reaction kinetics and of the hydrogenation activity of the commercial catalysts, under the conditions prevailing in the real hydrotreators. Since hydrogenation reactions are slowest, by the time they are taking place, the final products of HDS, HDN and HDO viz. hydrogen sulfide, ammonia and water are already present in reaction atmosphere. It is of great industrial importance to know the effects of these compounds on hydrogenation of aromatic hydrocarbons.

In this study, propylbenzene is selected as a model compound to observe the individual as well as the simultaneous effects of the presence of hydrogen sulfide, ammonia and water on the kinetics of its catalytic hydrogenation under industrial reaction conditions. Propylbenzene was selected because it and propylcyclohexane are the principal reaction products formed by the hydrodenitrogenation of quinoline, a model compound which have been studied extensively. It is representative of six-membered heterocyclic nitrogen compound encountered in practice.

Objectives of the Thesis:

The specific objectives of this thesis are as follows:

(1) Construction and testing of high-pressure, reactor system for studying catalytic hydro-processing reactions.

(2) Investigation of the best operating conditions of the Gas Chromatograph to analyze the reaction products.

(3) Study of the individual and simultaneous effects of the presence of hydrogen sulfide, ammonia and water on the kinetics of catalytic hydrogenation of

propylbenzene.

(4) Comparison of hydrogenation activity of oxide and sulfided forms of $NiMo/Al_2O_3$ commercial hydrotreating catalyst.

Chapter II

LITERATURE REVIEW

This chapter presents a review of literature of several important background subjects pertinent to this study. The emphasis is on model compound studies of aromatic hydrogenation over hydroprocessing catalysts. Brief descriptions about hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, hydrodemetallation and hydroprocessing catalysts are also included.

2.1 Hydrogenation of aromatics:

The literature of catalytic hydroprocessing provides only fragmentary and qualitative information about the reaction network, kinetics and reactivities of aromatic hydrocarbons. Most of the work has been done with unsupported and unpromoted catalysts and at conditions removed from those of industrial interest. Weisser and Landa (1973) compiled most of the information concerning the unpromoted and unsupported catalysts, with copious references. Their book is a valuable source in understanding the reactions involved on the sulfided catalysts.

The reported kinetics data for the aromatic hydrogenation in the presence of promoted sulfided

catalysts like $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$ are limited. Most of these studies were associated with simultaneous hydrodesulfurization, hydrodenitrogenation and/or hydrodeoxygenation. In only a few cases model compounds were used as feed stocks to provide understanding of the catalytic chemistry and kinetics of aromatic hydrogenation. Most of the studies are related to catalyst development, the emphasis being on product selectivities obtained with different catalysts under standard operating conditions; only a few studies were aimed at determining reaction kinetics, mechanisms, or relative reactivities. However, these studies provide important insights into the catalysis of various hydroprocessing reactions, including hydrogenation, especially the effects of support and promoter.

The hydroprocessing catalysts used in industry are promoted supported catalysts. The catalyst being used in the present study is nickel-promoted molybdenum catalyst on a γ-Al_2O_3 support; hence the attention here is focused on the promoted supported catalysts. The important studies related to this work on the unpromoted and unsupported catalysts are also included.

2.1.1 Hydrogenation of aromatics catalyzed by hydrotreating catalysts:

Ahuja et al. (1970) studied the hydrogenation of a feed containing toluene, cyclohexene and thiophene in a fixed bed reactor at 60 atm. and 350 °C. Their aim of experiments was to study the influence of metals from Group VIII (Co and Ni) on metals from Group VIA (Mo and W) and the effect of support. Various catalysts studied were sulfides of nickel, cobalt, molybdenum and tungsten; supported on silica, alumina or silica-alumina. The maximum hydrogenating activity is obtained at Group VIII metal/ Group VIA metal ratio of 0.33. The nickel-tungsten pair gives the highest hydrogenating activity. It was concluded that isomerization reactions are due to support, hydrogenation due to metals, whereas both support and metals play a role in hydrodesulfurization.

A rate expression for toluene hydrogenation has been presented by Ahuja et al. (1970), which has the following form:

$$r = \frac{k\, K_T P_T\, K_{H_2} P_{H_2}}{(1 + K_T P_T + K_C P_C + K_{Th} P_{Th} + K_{H_2S} P_{H_2S})^2}$$

where subscripts are as follows

T = toluene, Th = thiophene, C = hydrocarbons,

H_2S = hydrogen sulfide, H_2 = hydrogen.

The data to which the above rate expression are fitted were not presented, nor did the authors report the values of the kinetic parameters in the above expression.

Voorhoeve and Stuiver (1971a) studied the kinetics of hydrogenation of cyclohexene and benzene on nickel-tungsten sulfide catalysts. A microflow reactor was employed at 48 atm. and 200-400 °C. Carbon disulfide was added in the feed in order to maintain the activity of the catalyst. Kinetics were reported in the form of psuedo-first order rate constants. Both hydrogenation of cyclohexene and benzene were first-order, indicating that the reaction rate is strongly dependent on the adsorption of the hydrocarbons. Simultaneous hydrogenation of cyclohexene, benzene and and carbon disulfide shows that the hydrogenation sites were blocked by hydrogen sulfide and more so by carbon disulfide. The Arrhenius curves were nonlinear, indicating an activation energy that depends on temperature. For cyclohexene hydrogenation, the activation energy drops from 22 to 15 kcal/mol as the temperature was increased from 300 to 400 °C. However, the activation energies were same for both bulk and supported catalysts. This suggests that the mechanism is not changing by dispersion of metals sulfides on supports.

Voorhoeve and Stuiver (1971b) studied the mechanism of hydrogenation of cyclohexene and benzene on nickel-tungsten sulfide catalyst. They attributed the hydrogenation activity of these catalysts to tungsten ions on the surface of the WS_2 crystallites. Comparision of catalyst with and without nickel corroborates this. Nickel is inserted into the WS_2 layer structure between adjacent sulfur layers and is likely to be ionized. The promoter effect is due to an increase in the electronic concentration in the WS_2 sheets, producing an increased number of active tungsten ions on the surface. This increase in the number of tungsten ions has been observed by Electron Spin Resonance (ESR) spectroscopy. Comparision of bulk and alumina-supported nickel-tungsten sulfides shows that the same kinds of active sites are present in the two catalysts. The alumina carrier has no effect on the intrinsic properties of the sites. However, they suggested that cyclohexene hydrogenation proceed on different sites than benzene hydrogenation.

de Beer et al.(1976) used a batch reactor to study the hydrogenation of benzene at 400 °C and atmospheric pressure. Sulfided NiW, NiMo, CoMo and CoW catalysts supported on several supports were employed in order to determine the effect of promoter and support on hydrodesulfurization, hydrogenation and isomerization.

Results were similar to those reported earlier by Ahuja et al.(1970). No kinetic expression was reported.

Benzene hydrogenation reaction at atmospheric and elevated pressures have recieved considerable attention as documented by Weisser and Landa (1973). It was observed that the most rapid reaction at high hydrogen partial pressure was benzene hydrogenation to cyclohexane, followed by isomerization giving methylcyclopentane. The slowest reaction was hydrocracking to paraffinic hydrocarbons. The cyclohexene intermediate was present in trace amounts, and the reaction paths were confirmed from radioactive studies with mixed benzene and cyclohexane feed.

The tracer studies indicated that isomerization proceeds through the cyclohexene intermediate, in agreement with the reaction scheme proposed by Ahuja et al. (1970). The isomerization reaction proceeds through a carbonium ion mechanism. The proton needed to form the carbonium ion is obtained from the catalyst surface (Weisser and Landa, 1973). These studies indicated the presence of Bronsted acidity on MoS_2 catalysts. Ahuja et al. (1970) also explained their isomerization results by considering carbonium ion intermediates, but catalysts used in those studies were supported on alumina, alumina-silica or silica, and the Bronsted acidity was attributed

to the support rather than metal sulfides. The nature of the acidity of sulfide catalysts, both supported and unsupported, is poorly understood.

Rollmann (1977) used a mixed feed containing large number of sulfur-, nitrogen- and oxygen-containing compounds with naphthelene, 2-methylnaphthalene, 2,3-dimethylnaphthalene and 1,2,4-trimethyl benzene. The reaction was carried out in a trickle-bed reactor using commercial HDS-2 and HDS-1441 catalysts at 20-100 atm. and 290-430 °C. At low WHSV, naphthalene approached equillibrium conversion to tetralin. Conversion data obtained for various feed components have been compared by assuming a first order reaction rate expression. Based on these comparisons and on data obtained for postulated intermediates in the hydrogenation of sulfur- nitrogen- and oxygen- containing compounds, the order of reactivity by chemical type was proposed as follows:

sulfides >> p-alkylphenols > benzothiophene > quinoline > o-alkylphenols $\sim$ indoles $\sim$ benzofurans $\sim$ naphthelene > dibenzofurans >> mononuclear aromatics.

This pattern clearly shows the ease of HDS, HDN and HDO compared to hydrogenation of aromatics.

Biphenyl hydrogenation has been studied by Espino et al. (1978), in conjunction with HDS of dibenzothiophene.

They used a trickle-bed reactor operating at 30 atm. and 300-350 °C. Catalyst was sulfide CoMo on SiO_2-Al_2O_3 support. Thiophene was added to maintain catalyst activity and tetralin was used as solvent. A rate expression describing biphenyl hydrogenation kinetics has been presented as :

$$r = \frac{k\, K_{BPH} P_{BPH}\, K_H P_H}{(1 + K_{BPH} P_{BPH} + K_{CHB} P_{CHB})(1 + K_H P_H)}$$

where subscripts are as follows:

BPH = biphenyl; CHB = cyclohexylbenzene and

H = hydrogen

Cyclohexylbenzene was observed to be only product. Biphenyl hydrogenation was slower compared to HDS of dibenzothiophene.

Patzer et al. (1979) selected 1-methylnaphthalene as a model compound for charecterization of coal liquefaction catalysts. Hydrogenation of 1-metylnaphthalene was carried out in trickle-bed reactor at 70 atm. and 315-400 °C. Ten different proprietary hydrotreating catalysts were used. Carbondisulfide was added to maintain the catalyst activity. The kinetics were represented by psuedo-first order rate constants. Dealkylation of 1-methylnaphthalene was observed, which was subsequently

converted to tetralin and then to decalin. The ratio of concentrations of tetralin and naphthalene in the product remains constant at about 0.5, being unaffected by changes in catalyst composition, feed flow rate and reaction temperature in the range of 315-400 °C. They attributed this result to an equillibrium approach between naphthalene and tetralin.

Bhinde (1979) carried out the studies with naphthalene at 35 atm and 350 °C with a presulfided $NiMo/Al_2O_3$ catalyst in a batch autoclave. Carbondisulfide was added to the feed in order to maintain the activity of sulfided catalyst. Naphthalene was hydrogenated to 1,2,3,4-tetrahydronaphthalene (tetralin) in what appeared to be equillibrium concentration. Tetralin was further hydrogenated to cis- and trans-decahydronaphthalene (decalin). Under the conditions of this study, isomerized products of the type methylindane were not observed, indicating the absence of isomerization reactions observed in benzene hydrogenation. Reaction rate was reported to follow pseudo-first order kinetics for each reaction. The reaction network, with the pseudo-first order rate constants, is shown in Figure 2.1.1. They also observed that nitrogen-containing compounds strongly inhibit naphthalene hydrogenation.

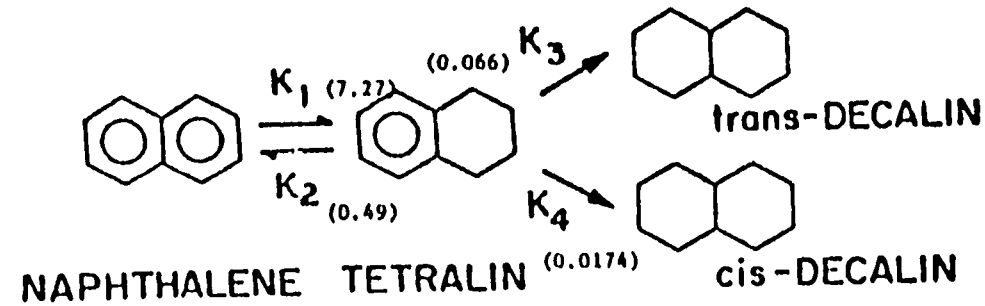


Figure 2.1.1 Reaction Network for Hydrogenation of Naphthalene in Batch Reactor (The numbers next to arrows are pseudo-first order rate constants in g.oil/gcat. min) Bhinde, 1979.

The primary product of naphthalene, tetralin, is a typical hydroaromatic structure, with one ring saturated and fused to a benzene ring. Hydroaromatics are important hydrogen-donor species, as they can easily give up hydrogen to acceptor species (e.g., free radical formed during coal liquefaction), and in turn are converted to aromatics. Tetralin is the most commonly used model compound, as a hydrogen donor, in coal-liquefaction experiments.

Richardo et al. (1979) studied the hydrogenation of phenanthrene in a mixed feed containing several nitrogen-, oxygen- and sulfur- containing compounds. They used a fixed-bed flow reactor operating at 70 atm. and 400 °C. Sulfided $NiOMoO_3$ on different commercial supports were used as catalysts. Under simultaneous processing, the main products of dibenzothiophene HDS was biphenyl; the main product of quinloine HDN was propylcyclohexane and that of dibenzofuran HDO was cyclohexylbenzene. This suggests that sulfur was removed without need for saturation of the sulfur-containing ring. For both nitrogen and oxygen removal, the ring containing the heteroatom was saturated before scission of carbon-nitrogen or carbon-oxygen bonds. Phenanthrene primarily produces hydrophenanthrenes which are excellent hydrogen donors, even better than tetralin. In order to compare

the catalyst performance, the apparent kinetic constants for the different reactions were evaluated from the conversion values assuming a pseudo-first order reaction mechanism and a plug flow pattern in the reactor.

Reactivities and reaction networks of hydrogenation of several aromatic hydrocarbons catalyzed by sulfided $CoMo/Al_2O_3$ were reported by Sapre and Gates (1981). Hydrogenation of benzene, biphenyl, naphthalene and 2-phenylnaphthalene was studied in a batch reactor at 75 atm. and 325 °C. Each reaction network involved reversible hydrogenation of the aromatic hydrocarbon (e.g. naphthalene) to give a hydroaromatic (e.g. tetralin) which experienced further slow hydrogenation (e.g. giving decalin). Slow isomerization reactions of cyclohexyl benzene to give methyl cyclopentylbenzenes were also observed. The quantitative kinetics data for the reaction network was presented by assuming that each reaction was pseudo-first order in hydrocarbon reactant. The reactivity of ring saturation was about an order of magnitude greater for (substituted) naphthalenes than for (substituted) benzenes.

A detailed kinetic study of biphenyl hydrogenation catalyzed by sulfided $CoMo/Al_2O_3$ was reported by Sapre and Gates (1982). They determined the rates of biphenyl hydrogenation from differential conversion data obtained

with a flow microreactor. Temperatures were 300-375 °C pressures were 70-100 atm., and concentrations of reactants and products were varied widely. Rate equations of the Langmuir-Hinshelwood type were developed to correlate differential conversion data for the hydrogenation of biphenyl. The rate equation that gave the most satisfactory fit to the data at all four temperatures (300, 325, 350 and 375 °C) was the folowing:

$$r = \frac{k\, K_{BPH} K_H^3 \left[C_{BPH} C_H^3 - (1/K_c) C_{CHB}\right]}{(1 + K_{BPH} C_{BPH} + K_{H_2S} C_{H_2S})^2 (1 + K_H C_H)^2}$$

The authors claim that this rate expression predicts both integral and differential data of biphenyl hydrogenation, obtained by different reactor geometries.

In a very recent publication, Gultekin et al.(1984) reported the results of their studies of the effects of hydrogen sulfide and ammonia on catalytic hydrogenation of propylbenzene. The experiments were carried out in a vapor phase continuous flow microreactor, containing a single charge of commercial presulfided $NiMo/Al_2O_3$ hydrotreating catalyst. Hydrogen sulfide and ammonia were generated, in situ, under reaction conditions by adding carbondisulfide and propylamine, respectively. Studies were made at 330, 350 and 375 °C at total pressures of

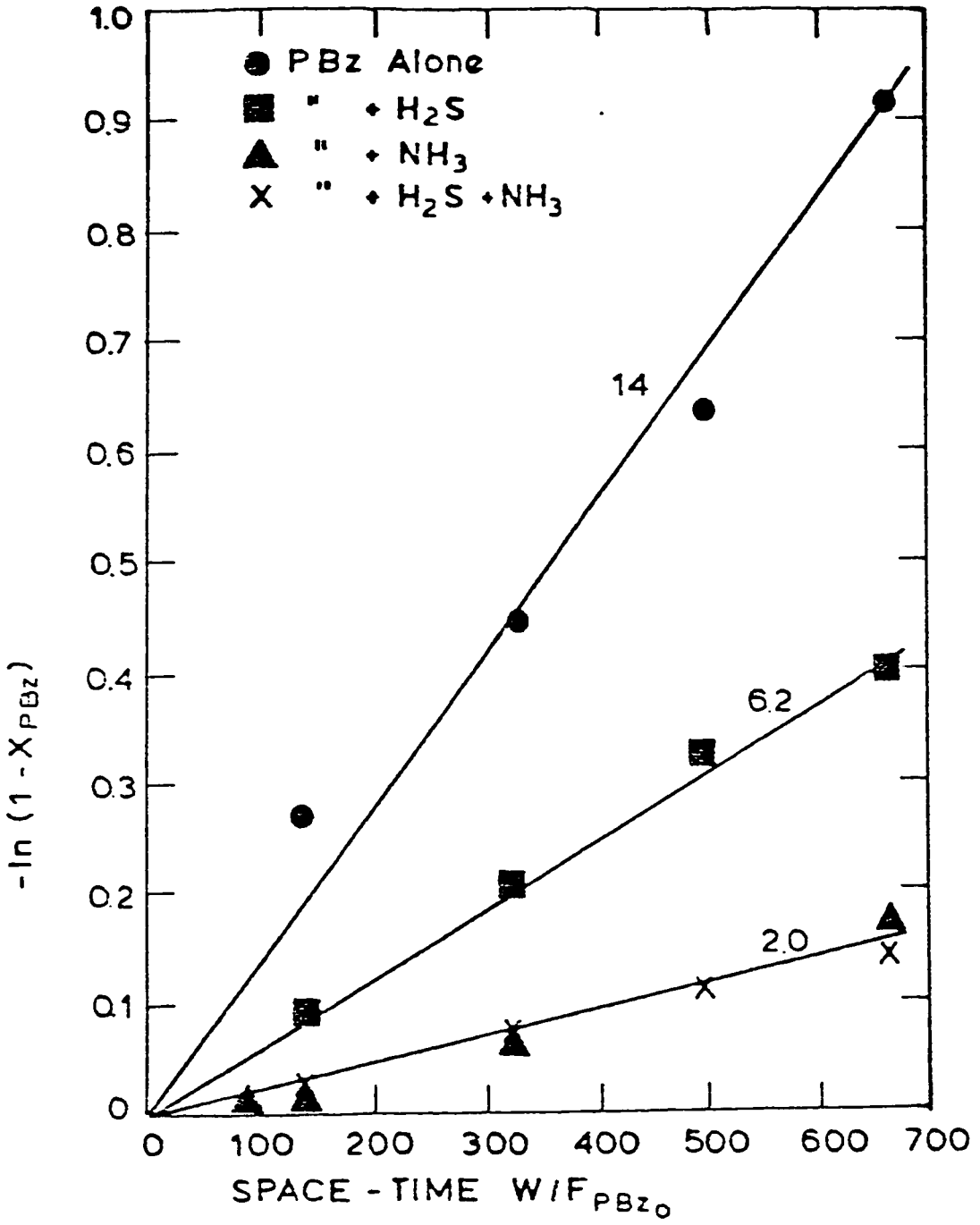


Figure 2.1.2 First Order Plot for Propylbenzene Hydrogenation at 375 °C and 6.9 MPa (Gultekin et al., 1984).

3.55 and 6.9 MPa. The partial pressures of propylbenzene, ammonia and hydrogen sulfide were 13.3 kPa each. Runs were carried out feeding propylbenzene alone with the hydrogen or propylbenzene plus a compound to generate hydrogen sulfide or ammonia, or both, in situ.

The hydrogenation of propylbenzene to propylcyclohexane was first order in propylbenzene for all feed mixtures studied. At 6.9 MPa and 375 °C the hydrogen sulfide decreased the rate by a factor of 2 and ammonia decreased it by a factor of 7. A mixture of hydrogen sulfide and ammonia behaved like ammonia alone. This is illustrated in Figure 2.1.2. No products other than propylcyclohexane, such as propylcyclohexene, were observed.

2.1.2 Hydrogenation of aromatics catalyzed by unsupported metal sulfides:

A review of hydrogenation with unpromoted and unsupported metal sulfide catalysts (e.g., MoS_2, WS_2) was compiled by Weisser and Landa (1973). The following brief summary of this subject is derived from their book.

Hydrogenation of the aromatic ring, which is stablised by mesomerism, is more difficult than that of substances which contain an isolated double bond in the carbon chain. When metal sulfides are used as typical high-temperature

catalysts a suffiently high reaction rate is achieved with hydrogenating aromatic substances at temperatures of at least 300 °C and at hydrogen pressures of 50-100 atm.

The hydrogenation mechanism of aromatic substances in the presence of sulfide catalysts is little known at present, and only its relationship to the geometrical factor has been partially clarified. According to Balandin's multiplet theory, adsorption of the benzene ring is assumed to take place on the surface of a suitable crystal lattice having the optimum distance between catalytic centres for hydrogenation of the aromatic ring. Typical hydrogenation catalysts are metals which crytallise in face-centred cubic or hexagonal lattices. This arrangment allows the sextet centre to be formed, which are active for hydrogenation. The true mechanism of hydrogenation is more complicated than would appear from the simple scheme of the multiplet theory.

Studies have shown that MoS_2 and WS_2 behave differently as hydrogenation catalysts. In autoclave experiments at high pressures (100-200 atm) and temperatures (380-475 °C), it was found that on WS_2 the relative hydrogenation rate of benzene and methyl-substituted benzenes is given by the following expression:

$$r_n = r_o\ (1.3 + n) \qquad n = 1 \text{ to } 5$$

Table 2.1.1

Differences for Benzene Hydrogenation on MoS_2 and WS_2 Catalysts

Catalyst	MoS_2	WS_2
Activation energy	19.3 kcal/mol	24.5 kcal/mol
Reaction order with respect to benzene	0.0	0.5
Reaction order with respect to hydrogen	1.0	1.5

Source: Weisser and Landa (1973).

where r_n is the relative rate of akylbenzene, r_o is the rate of benzene, and n is the number of methyl substituents on the aromatic nucleus.

The relationship does not apply to the MoS_2 catalyst, although its properties are similar to those of the WS_2 catalyst. Table 2.1.1 summarizes the differences observed for the benzene hydrogenation on the MoS_2 and WS_2 catalysts. There is no satisfactory explanation for this discrepancy.

The relative hydrogenation rates for different aromatic compounds on MoS_2 and WS_2 catalysts under comparable conditions are summarized in Table 2.1.2. Monolefins are hydrogenated several orders of magnitude more than aromatic substances, whereas the rates of hydrogenation of condensed linearly annulated aromatic compounds are considerably higher than monoaromatic compounds (on WS_2, naphthalene is hydrogenated 23 times, anthracene 62 times more quickly than benzene). It has been argued by Weisser and Landa (1973) that the contribution of resonance energy of each additional benzene ring to an aromatic molecule is less than the resonance energy of the isolated benzene ring. This result suggests that the annulated aromatic molecules are less aromatic in charecter, and the aromaticity per benzene ring decreases with increasing number of rings.

Table 2.1.2

Relative Hydrogenation Rates of Aromatics on MoS_2 and WS_2 Catalysts

Reactant	Product	Relative Hydrogenation Rate*	
		MoS_2	WS_2
Benzene	Cyclohexane	100	100
Toluene	Methylcyclohexane	99	230
m-Xylene	1,3-Dimethylcyclohexane	108	330
Ethylbenzene	Ethylcyclohexane	78	130
1,2,4-Trimethylbenzene	1,2,4-Trimethylcyclohexane	111	430
Pentamethylbenzene	Pentamethylcyclohexane	92	606
Hexamethylbenzene	Hexamethylcyclohexane	---	150
Naphthalene	Tetralin	1409	2300
Tetralin	Decalin	287	250
Anthracene	9,10-Dihydroanthracene	---	6210
9,10-Dihydroanthracene	Tetrahydroanthracene	---	1380
Tetrahydroanthracene	Octahydroanthracene	---	460
Octahydroanthracene	Perhydroanthracene	---	299
Chrysene	Tetrahydrochrysene	---	80
Tetrahydrochrysene	Octahydrochrysene	---	75
Octahydrochrysene	Dodecahydrochrysene	---	95

*High pressure hydrogenation, temperature around 400 °C.

Source: Weisser and Landa (1973).

Angularly annulated chrysene, however, is hydrogenated relatively slowly, presumably due to steric restrictions of adsorption on the catalyst surface. Another regular feature of aromatic hydrogenation is a decrease of reaction rate with the degree hydrogenation of the initial polycyclic series, as is evident by the anthracene series (Table 2.1.2).

2.2 Hydrodesulfurization:

Sulfur is present largely in the form of thiols (mercaptans), sulfides, disulfides and thiophenes. Thiols are the most reactive and thiophenes are the least reactive; the reactivity of thiophenes decreases with increase in the number of aromatic rings.

The literature concerning hydrodesulfurization has been reviewed in detail by Schuman and Shalit (1970) and by Schuit and Gates (1973). More recent reviews are by Mitchell (1977) and by Gates et al. (1979). A brief review of literature on hydrodesulfurization of model compounds is presented in this section.

Thiophene hydrodesulfurization have been studied extensively by Owens and Amberg (1961 and 1962) and by Desikan and Amberg (1963 and 1964). The catalysts were commercial $CoMo/Al_2O_3$, chromia and several molybdenum

sulfides. Kinetics data were obtained from a pulse microreactor operated at low conversions. The initial step in HDS is the direct extrusion of sulfur to form butadiene, which undergoes hydrogenation to 1-butene rapidly. 1-Butene is then isomerized to cis- and trans-2-butene or further hydrogenated to butane. They also observed that hydrogen sulfide inhibited the HDS of thiophene and the hydrogenation of butene, but it had only little effect on isomerization. These results led them to suggests that more than one kind of active site is operative in HDS.

Kinetic studies of HDS of compounds found in very light distillates has been reported by Phillipson (1971). The catalyst was $CoMo/Al_2O_3$. Vapor feed contain heptane mixed with dimethyl sulfide, phenyl mercaptan, diethyl sulfide, tetrahydrothiophene or thiophene. The data was represented by an empirical rate equation, which shows a dependence of rate on total pressure and indicates inhibition by the hydrocarbon heptane;

$$r_{HDS} = \frac{k\, P_S (P_{H_2} P_{tot})^{0.5}}{P_{HC}^{0.5}[1 + 0.21(P_{H_2S}/P_{tot})]}$$

This rate expression is difficult to justify on theoretical grounds. However, the results were valuable in demonstrating relative lack of reactivity of thiophene

compared with mercaptans, sulfides and disulfides.

Satterfield and Roberts (1968) performed a kinetic study of thiophene hydrodesulfurization at atmospheric and 235-265 °C on a commercial $CoMo/Al_2O_3$ catalyst in a differential reactor. The reaction was inhibited by hydrogen sulfide. The rate was described by a Langmuir-Hinshelwood type of kinetic expression as follows:

$$r = \frac{k P_T P_H^n}{(1 + K_T P_T + K_S P_S)^2}$$

(The subscipt T refers to thiophene, S to hydrogen sulfide and H to hydrogen). This expression is consistent with the earlier results of Frye and Mosby (1967). This and other studies indicate that the HDS and hydrogenation occur on different sites. The HDS reaction appears to be between half and first order with respect to hydrogen and first order in the concentration of thiophene. The HDS was inhibited by hydrogen sulfide and more severly inhibited by basic nitrogen compounds.

Gultekin (1981) studied the effect of methyl substitution on hydrodesulfurization of thiophene on sulfided $NiMo/Al_2O_3$ catalyst using a flow microreactor. Comparision of HDS of thiophene, 2-methyl thiophene and 2,5-dimethylthiophene, under same reaction conditions

resulted in the order of reactivity as

thiophene > 2-methylthiophene > 2,5-dimethylthiophene

This order shows that the steric hinderance effects of methyl groups at α-position were more important than inductive effects. The results also showed that HDS of 2-methyl thiophene to that of 2,5-dimethyl thiophene.

The importance of three- and four-ring sulfur-containing compounds is that they are not only present in petroleum residua and synthetic crudes, but also that they are among the least reactive. The relative reactivties of thiophenic compounds at high pressure was studied by Nag et al. (1979). Their results are summarized in Table 2.2.1.

Givens and Venuto (1970) studied the reaction network involved in the HDS of substituted benzothiophenes. Conversion data were obtained in a steady-state flow reactor packed with particles of a commercial $CoMo/Al_2O_3$ catalyst. They ruled out desulfurization reactions involving C-C bond breaking, as the corresponding product was not formed. Saturation of aromatic ring was found not to be necessary for breaking bond between sulfur and aromatic carbon to occur. Using appropriate intermediates as feeds, Givens and Venuto (1970) demonstrated that primary sulfur extrusion, alkyl migration on the

Table 2.2.1

Comparision of Reactivities of Thiophinic Compounds

Reactant	Pseudo-first Order Rate Constant (cc/gm.cat. hr.)
Thiophene	4980
Benzothiophene	2920
Dibenzothiophene	220
Benzonaphthothiophene	580
7,8,9,10-Tetrahydro-benzonaphthothiophene	280

Reaction Conditions: 300 °C, 71 atm, presulfided $CoMo/Al_2O_3$

Source: Nag et al., 1979.

thiophenic ring, and the dealkylation of the thiophenic ring all occur during HDS of 2-methyl benzothiophene at 400 °C and at atmospheric pressure.

Kilanowski and Gates (1980) studied the kinetics of HDS of benzothiophene in a steady-state differential flow microreactor containing particles of sulfided $CoMo/Al_2O_3$ catalyst. The only hydrocarbon formed in more than trace amounts was ethylbenzene, showing that there was no ring saturation. Kinetic results demonstrate that competative adsorption of benzothiophene and hydrogen sulfide on one kind of catalytic site and of hydrogen on another. Benzothiophene is found to be twice as active as thiophene and a comparision of kinetic results of two reactants suggests a similarity in the mechanisms of their reactions. Catalytic deactivation was negligible over hundreds of hours of operation. Rate expressions of the Langmuir-Hinshelwood type were tried, but no single equation gave a good fit at all three temperatures studied. HDS of dibenzothiophene was studied by Houalla et. al. (1978).

A detailed reaction network of HDS of dibenzothiophene over sulfided $CoMo/Al_2O_3$ at 300 °C and 100 atm. is shown in Figure 2.2.1. Broderick and Gates (1980 and 1981) performed a thorough kinetic study of HDS of dibenzothiophene catalyzed by sulfided $CoMo/Al_2O_3$ at high

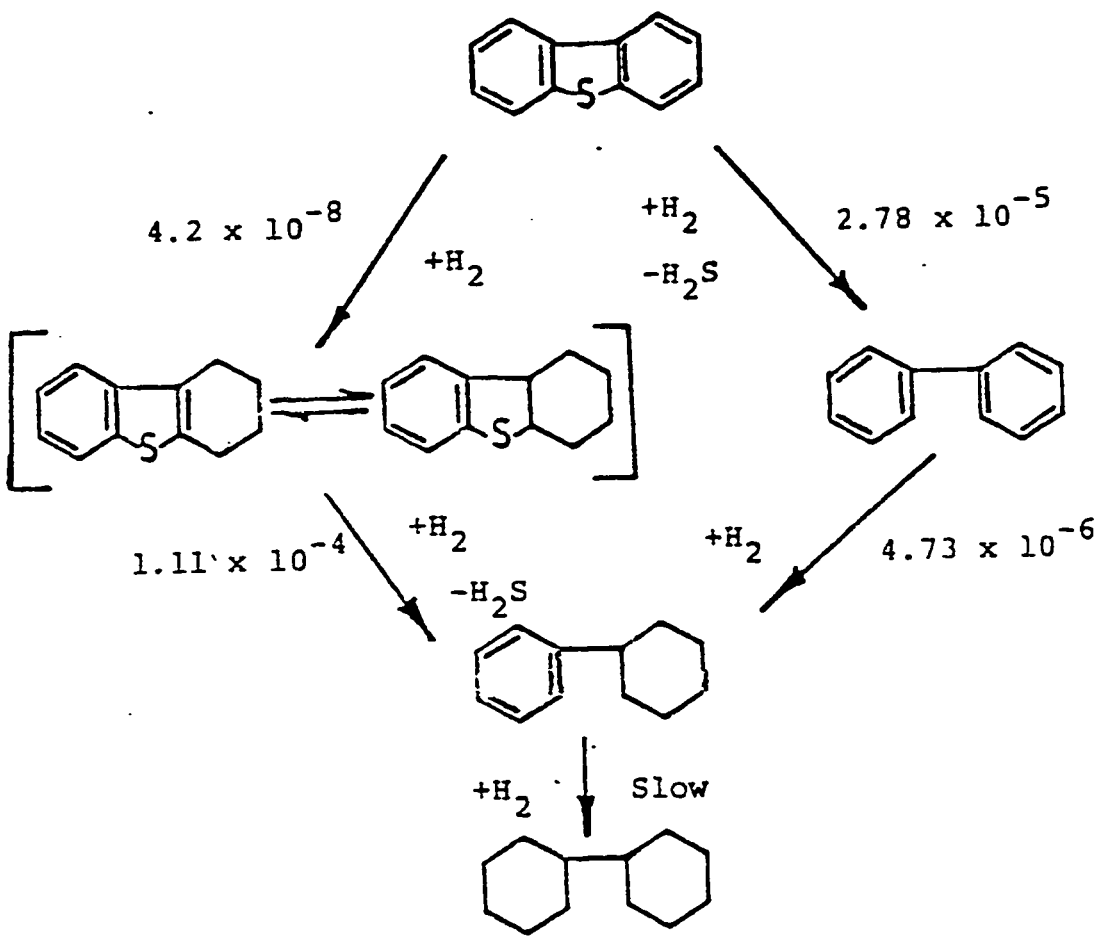


Figure 2.2.1 Reaction Network for HDS of Dibenzothiophene. (The numbers next to arrows are pseudo-first order rate constants in units of m^3/kg.cat. sec) Houalla et al.

pressures (30-150 atm.) They concluded that dibenzothiophene undergoes two parallel reactions:

(a) hydrogenolysis to give biphenyl, and
(b) hydrogenation to give an equillibrium mixture of two reactive intermediates.

Rapid hydrogenolysis of these intermediates gives cyclohexylbenzene. Biphenyl is further hydrogenated to give cyclohexylbenzene and bicyclohexyl, but much more slowly. The rate of hydrogenolysis is higher than the rate of hydrogenation at hydrogen sulfide concentrations near zero and/or at temperatures greater than 300 °C; direct sulfur removal is favored. The rate data for hydrogenolysis and for hydrogenation were fitted to equations of the Langmuir-Hinshelwood type.

HDS of methyl sustituted dibenzothiophenes was studied by Houalla et al. (1980) and deduced that the rate is greatly affected by the position and number of methyl groups attached. Methyl groups can increase the HDS activity by electron donation effect and decrease due to steric effects.

Sapre et al. (1980) studied the HDS of benzo-naphtho-thiophene catalyzed by sulfided $CoMo/Al_2O_3$ catalyst, in a batch reactor. At 300 °C and 70 atm., the sulfur-containing reactant underwent hydrogenation of benzoid

rings and hydrogenolysis of carbon-sulfur bonds at approximately equal rates. The quantitative kinetics data for the reaction network was represented by assuming each reaction as psuedo first order in the reactant.

2.3 Hydrodenitrogenation:

A wide variety of heterocyclic nitrogen compounds are present in petroleum residua and in synthetic crudes. Pyrrole, pyridine, piperidine, quinoline, indole, indoline, carbazole, acridine and benzacridine are the main heterocyclic nitrogen compounds.

Excellent reviews of the earlier literature on HDN of oil fractions and of model compounds has been given by Mayer (1974) and by Goudriaan (1974). A recent survey is by Katzer and Sivasubramanian (1979). The survey given in this section is limited to model compound studies, but include the more recent reports.

In their classical paper, "How easy is hydrodenitrogenation ?", Flinn et al. (1963) concluded that nitrogen compounds containing aromatic type heterocyclic ring, such as quinoline, are more difficult to hydrodenitrogenate. They also found that several organic nitrogen-containing compounds, including quinoline, indole, n-butylamine and aniline, followed pseudo first

order kinetics. The ring hydrogenation reaction was reported to be the rate limiting step in the hydrodenitrogenation.

Doelman and Vlugter (1963) studied the quinoline HDN reaction over a prereduced $CoMo/Al_2O_3$, and concluded that rapid hydrogenation of quinoline on the heterocyclic ring occurs first, followed by ring rupture and deamination.

Cox (1961) studied HDN of five- and six-membered ring heterocyclic nitrogen compounds. He found that nitrogen removal was first order with respect to nitrogen in six-membered rings whereas five-membered rings exhibited second order dependency.

McIlvried (1971) showed that for the catalytic HDN of pyridine at high pressures the reaction scheme is

$$\text{pyridine} \xrightarrow{a} \text{piperidine} \xrightarrow{b} \text{pentylamine} \xrightarrow{c}$$

$$\text{pentane} + \text{ammonia}$$

He reported that at 315 °C and 50-100 atm, step b is rate limiting, the rate of this step obeying Langmuir-Hinshelwood kinetics.

Sonnemans et al.(1972) studied the HDN of pyridine on a MoO_3 catalyst (oxide form). They reported that the reaction network is much more complex than the one

proposed by McIlvried. They stressed the importance of disproportionation reactions and suggested that piperidine is converted to N-pentylpiperidine before complete denitrificaion. Their main conclusions are: ring hydrogenation influences the denitrogenation rate at temperatures below about 300 °C; cracking and hydrocracking reactions are rate-limiting at temperatures higher than 400 °C.

Aboul-Gheit and Abdou (1973) employed a batch reactor system and oxidic $CoMo/Al_2O_3$ catalyst for HDN studies of quinoline and other model nitrogen compounds. Nitrogen removal from quinoline was reported to follow pseudo-first order kinetics, with an activation energy of 30 kcal/mol. The authors concluded that hydrogenolysis of heterocyclic ring in Py-tetrahydroquinoline was the rate determining step in the rate determining step in quinoline HDN and postulated that the basicity of nitrogen compounds plays a role in their HDN mechanism.

Goudriaan (1974) performed an extensive study of HDN of pyridine. Both oxide and sulfide form of $CoMo/Al_2O_3$ catalyst were used. Individual effects of hydrogen sulfide and water vapor were also studied. A two-step kinetic model was proposed, describing the HDN of pyridine in terms of consecutive first-order reactions:

pyridine $\longrightarrow$ 'intermediate' $\longrightarrow$ ammonia.

The presence of hydrogen sulfide inhibits the hydrogenation of pyridine to piperidine. With oxide catalyst, water vapor caused a marked decrease in ring hydrogenation activity, whereas with sulfided catalyst presence of water vapor did not affect ring hydrogenation activity. However, in the presence of hydrogen sulfide, hydrogenolysis rate increases by a factor of about four. He also concluded that ring hydrogenation and hydrogenolysis require different sites on the catalyst surface.

Shih et al. (1977) investigated the kinetics of quinoline HDN in a batch liquid phase (slurry) reactor using sulfided $NiMo/Al_2O_3$ catalyst and a paraffinic white oil as carrier liquid. Quinoline was rapidly hydrogenated to an equillibrium concentration of 1,2,3,4-tetrahydroquinoline, but the other hydrogenation reactions as well as the hydrogenolysis reactions were reported to be kinetically limited. The rates of these reactions were described by first-order kinetics. They interpreted the rate by a Langmuir-Hinshelwood kinetic model in which hydrogen and nitrogen compounds compete for active catalyst sites, and all nitrogen compounds have comparable adsorption constants. The hydrogenation reactions were reported to be second order in hydrogen, but the

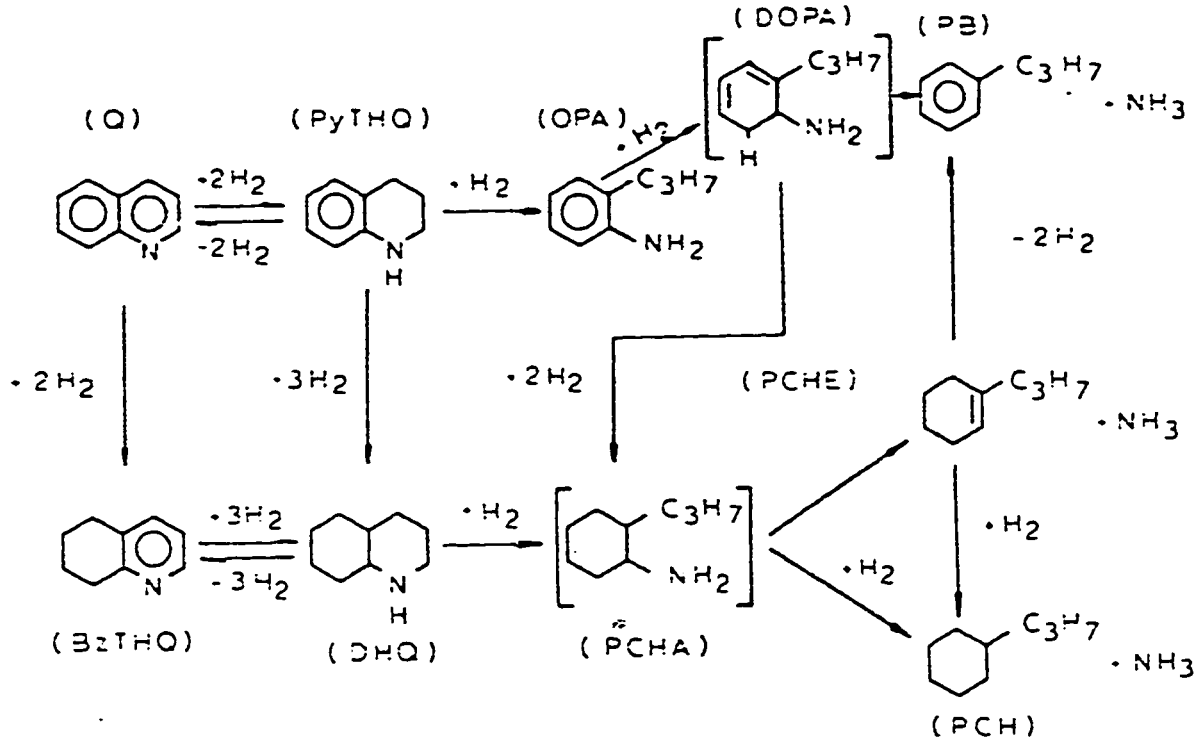
hydrogenolysis reactions were of lower order in hydrogen. It was concluded from kinetic analysis that nitrogen removal occured primarily through the 5,6,7,8-tetra-hydroquinoline and decahydroquinloine intermediates. The effects of different catalysts, presulfiding and hydrogen sulfide on quinoline HDN were also investigated (Shih et al., 1978). Presulfided $NiMo/Al_2O_3$ was better catalyst for nitrogen removal than presulfided $CoMo/Al_2O_3$ or NiW/Al_2O_3. Sulfided $NiMo/Al_2O_3$ was about twice as active as the oxidic form for nitrogen removal. The presence of hydrogen sulfide in the reaction environment, even with a presulfided catalyst, increased the rate of nitrogen removal.

The thermodynamic equillibria of selected heterocyclic nitrogen compounds with their hydrogenated derivatives have been reported by Cocchetto and Satterfield (1976). It was concluded that, under HDN reaction conditions, hydrogenolysis of C-N bonds is essentially irreversible, while initial saturation of heterocyclic rings is potentially reversible or thermodynamically limited.

Satterfield et.al. (1978) studied the intermediate reactions in quinoline HDN over a presulfided $NiMo/Al_2O_3$ catalyst, in a continuous vapor-phase reactor. Under all reaction conditions investigated, quinoline was rapidly hydrogenated to an equillibrium concentration of 1,2,3,4-

tetrahydroquinoline. The dominant initial reaction pathway was reported to vary with temperature. At lower temperatures, the concentration of quinoline was much less than that of 1,2,3,4-tetrahydroquinoline, and the later was converted to either o-propylaniline or decahydroquinoline. At higher temperatures, the equillibrium concentration of quinoline relative to 1,2,3,4-tetrahydroquinoline was greatly increased, and the conversion rate of quinoline to 5,6,7,8-tetrahydroquinoline subsequently to decahydroquinoline became significant.

Satterfield and Cocchetto (1981) studied the reaction network and kinetics of vapor phase catalytic HDN of quinoline in a flow microreactor packed with presulfided $NiMo/Al_2O_3$ catalyst. The reaction network for quinoline HDN is shown in Figure 2.3.1. The results indicated that the initial ring saturation reactions of quinoline are reversible; also, saturation of the aromatic ring is thermodynamically more favorable than saturation of the heterocyclic ring. Nitrogen removal occured primarily through the decahydroquinoline intermediate, and propylcyclohexane was the major hydrocarbon product. Adsorbtivities of the nitrogen compounds in the quinoline HDN network varied significantly. A Langmuir-Hinshelwood kinetic model, allowing for these different



Q	quinoline
PyTHQ	Py (or 1,2,3,4)-tetrahydroquinoline
BzTHQ	Bz (or 5,6,7,8)-tetrahydroquinoline
DHQ	decahydroquinoline
OPA	o-propylaniline
PCHA	propylcyclohexylamine
PB	propylbenzene
PCHE	propylcyclohexene
PCH	propylcyclohexane
DOPA	dihydro o-propylaniline

Figure 2.3.1 Reaction Network for HDN of Quinoline in the Presence of Hydrogen Sulfide (Gultekin, 1980).

adsorbtivities, was developed for the hyrogenolysis and nitrogen removal reactions. On active catalyst sites, the 1,2,3,4-tetrahydroquinoline and decahydroquinoline reaction intermediates appeared to adsorb about six times as strongly as the less basic aromatic amines (quinoline, 5,6,7,8,-tetrahydroquinoline and o-propylaniline), which in turn showed an adsorption strength approximately four times greater than that of ammonia.

Gultekin (1980) studied the effect of hydrogen sulfide on the kinetics of HDN of quinoline and its reaction intermediates in vapor phase. The results are summarized in the paper by Satterfield and Gultekin (1981). It was observed that there was a decisive enhancement effect of hydrogen sulfide on the nitrogen removal from heterocyclic nitrogen compounds, whereas there was a slight inhibition in HDN of o-propylaniline. Upon increase of partial pressure of hydrogen sulfide, nitrogen removal was enhanced up to a limiting value above which further increase of partial pressure of hydrogen sulfide had little effect. The HDN of nitrogen compounds was represented by a Langmuir-Hinshelwood type of kinetic expression in which different adsorbtivities were utilized for different groups of nitrogen compounds. The kinetic analysis showed that decahydroquinoline and 1,2,3,4-tetra-hydroquinoline adsorb six times more strongly than

quinoline, 5,6,7,8-tetrahydroquinoline and o-propylamine, whereas ammonia adsorbs twenty four times less strongly than heterocyclic compounds. At standard HDN conditions (1000 psi, 375 °C), hydrogen sulfide inhibited the hydrogenation steps by about 10-15%, but enhanced the hydrogenolysis steps by a factor of about 2 to 5.

Satterield and Carter (1981) studied the effects of water vapor on the catalytic HDN of quinoline. It was observed that water vapor moderately accelerates certain reactions in the HDN network and moderately inhibits others. There was little net effect on the overall HDN rate at 330 and 375 °C and a slight inhibiting effect at 420 °C. Water vapor slightly increases the degree of saturation of hydrocarbons and slightly decreases it at 420 °C. The marked enhancing effect of hydrogen sulfide on the HDN rate is not significantly affected by the presence of water vapor.

Satterfield and Yang (1984) recently published results of their studies of catalytic HDN of quinoline in a trickle-bed reactor and compared the results with the vapor phase reaction. Using quinoline or various reaction intermediate reaction products, they showed that the reaction rate constants for the various HDN reactions in the presence of inert paraffin liquid (hexadecane) are very similar to those for the same reactions in the vapor

phase, although the liquid tends to equalize the adsorbtivities of the various nitrogen compounds present. Over a wide range, for a specified pressure and temperature, the percent conversion as a function of contact time is remarkably similar for liquid- and vapor-phase processing. In both cases, the overall HDN reaction is essentially zero order under the conditions studied. Equillibrium between quinoline and 1,2,3,4-tetrahydroquinoline was rapidly attained in both vapor phase and liquid phase processing.

Yang and Satterfield (1984) studied the effect of hydrogen sulfide on the catalytic HDN of quinloine in a trickle-bed reactor and compared the results with vapor phase studies of Satterfield and Gultekin (1981). They observed that the presence of hydrogen sulfide in the overall reaction network somewhat inhibits hydrogenation and dehydrogenation steps markedly accelerates the hydrogenolysis reactions. However, there was a net increase in the overall rate of HDN. These effects are similar to those observed in vapor-phase reactions.

2.4 Hydrodeoxygenation:

The most important oxygen-containing species present in synthetic liquids are phenols and furanic rings containing

heterocyclic compounds. In a detailed analysis of an anthracene oil, Scheppele et al. (1981) reported that 81% of the acids were hydroxylated aromatics. Carbonyl and carboxyl groups are also found. In liquids derived from coal and biomass, the content of oxygen heteroatom is markedly higher than that of nitrogen and sulfur.

An extensive literature exists on HDS and on HDN, but relatively little attention has been paid as to how oxygen species may affect HDS/HDN or the nature of the reaction networks of HDO; although HDO is one of the major reactions occuring during hydroprocessing. This may be because oxygen is not a significant component in petroleum. This section reviews the available literature on HDO.

In HDO of phenol over MoS_2 catalyst (Weisser and Landa, 1973), hydrogenation of benzene ring is far more dominant than hydrogenolysis of the phenolic hydroxyl group at high pressures (about 100 atm). The dehydration of cyclohexyl alcohol is by far the most rapid reaction under these conditions.

Rollmann (1977) studied the simultaneous HDS, HDN and HDO reactions occuring in a mixture of several model compounds on sulfided $CoMo/Al_2O_3$. Dibenzofuran was used as a representative oxygen compound in the model

feedstock. He further determined the reactivity of several other phenol and furan derivatives by substituting them one at a time for dibenzofuran in the model mixture. He concluded that alkyl phenols are more reactive than dibenzofurans.

Furimsky (1978 and 1979) studied the HDO of a heavy hydrocracked gas oil. A 345-525 °C hydrocracked gas oil from thermal hydrocracking of Athabasca bitumen was catalytically hydrotreated over a series of catalysts. Unpromoted and promoted molybdate catalysts supported on alumina were used. The extent of oxygen removal was by no means complete even at high temperatures and the observed results are related to the chemical composition of catalysts. Deoxygenation increases with concentration of MoO_3 up to about 6 wt%. Futher increase in the MoO_3 concentration do not appreciably increase oxygen removal. Deoxygenation is further enhanced by the addition of cobalt and nickel oxides to the molybdate catalysts. Independent acidity measurements on the liquid products suggests the presence of phenols.

Krishnamurthy et al. (1981) performed a kinetic study of the catalytic HDO of dibenzofuran on presulfided $NiMo/Al_2O_3$ catalyst. All experiments were carried out in an one-liter batch autoclave. Based on the reaction intermediates identified, a reaction network for HDO of

dibenzofuran was established. The rate constants for the various steps in the network were estimated assuming all the reactions to be first order in the reactant. The effects of temperature in the range of 343-376 °C and hydrogen pressure in the range of 1000-2000 psig. were examined upon the individual steps. The removal of oxygen from dibenzofuran under the above conditions proceeded via direct extrusion as well as through the formation of hydrogenated intermediates, with the catalyst showing selectivity towards the latter mode. Presulfiding the catalyst as well as the addition of carbondisulfide, to maintain a partial pressure of hydrogen sulfide during reaction, enhanced the activity of catalyst. The effect of initial concentration of dibenzofuran indicated a retarding influences on its HDO. The HDO of two key reaction intermediates, namely, o-phenylphenol and cyclohexylphenol was also investigated. The primary mode of oxygen removal from both the phenols was through the formation of highly reactive hydrogenated intermediates. The rates of decomposition of these phenols were fairly rapid and highly temperature sensitive, thereby explaining their absence in the reaction products of dibenzofuran HDO.

Mechanism of catalytic HDO of tetrahydrofuran was investigated by Furimsky (1983). The reactions were

carried out in a continuous microreactor. Product distribution during the HDO of tetrahydrofuran depends on catalyst pretreatment. Butenes were the major products in the presence of sulfided catalyst, while butadiene and propylene were predominant over the reduced catalyst. Approximate surface reaction routes were proposed to account for the observed differences. The formation of carbonaceous deposits was observed during HDO of tetrahydrofuran.

2.5 Hydrodemetallation:

A well recognized problem associated with the upgrading of petroleum residuals is the presence of trace metals, chiefly nickel and vanadium. These contaminations tend to accumulate on catalysts during processing, decrease catalyst effectiveness, and lead ultimately to irreversible deactivation.

Ali et al. (1983) analyzed samples of crude petroleum from nine different fields of Saudi Arabia for 17 trace metals. Atomic Absorption Spectrometry was used for the purpose. For each of the ten crude oils investigated, the most abundant trace metals observed were vandium and nickel. Vanadium and nickel concentration ranged from 2 to 60 ppm and 0.5 to 17 ppm, respectively. Other metals,

i.e., aluminum, calcium, cadmium, chromium, iron, manganese, lead and zinc were present at the 0.5-7 ppm level. The V/Ni index ranges from 2.78 to 4.35.

The metals problem has been extensively researched in the past. Among the numerous approaches taken, one can cite the development of catalysts with increased resistance to metals poisoning, the use of ebullated beds, and the direct removal of metals from feedstocks by various physical and chemical means.

One of the more practical methods for feedstock demetallation is the use of pretreatment gaurd-chambers containing solid adsorbents. The feasiblity of guard-chamber technique depends on the availablity of adsorbents having pore structures which will not impede the diffusion of the metal-containing asphaltene colloids (10-100 °A diameter), and which are inexpensive enough to be discarded after a single cycle. Activated bauxite has been mentioned in this regard as a cheap naturally occuring adsorbent. Maganese nodules, another naturally occuring mineral, have been found to be active for the demetallation of topped crude in the presence of hydrogen, as reported by Chang and Silvestri (1974).

Chang and Silvestri (1976) studied the catalytic activity of Lake Michigan maganese Nodules (LMN) for

demetalation of various petroleum residuals. Experiments were carried out in high-pressure, trickle-bed microreactors containing 20-100 cc of catalyst. The influence of hydrogen pressure on the aging charecterstics of the LMN catalyst was compared against a commercial $CoMo/Al_2O_3$ catalyst and an activated bauxite (Porocel). The LMN catalyst was found to have a comparitively lower aging rate as the hydrogen pressure was reduced below 2000 psig. This was attributed to its unusual macropore structure.

Oleck and Sherry (1977) evaluated fresh water maganese nodules and CoMo on wide pore alumina as catalysts for demetalation and desulfurizing petroleum residua. The effects of temperature, hydrogen pressure and reaction time were explored. The results were represented by second-order kinetics, however they mentioned that if the metal complexes in residual oils are divided into two groups, each follows first-order kinetics.

Riley (1978) studied the effect of catalyst properties on heavy feed hydroprocessing. He showed that the nickel and vanadium removal follows first-order kinetics and that the vanadium species are more reactive than nickel. Also, that the demetallation reactions are significantly more rapid than nitrogen removal. Pore structure of the catalyst is the controlling parameter for metals removal.

There was a significant difference in the mechanism for catalyst having pore diameters smaller than 100°A, as compared to catalysts having pore diameters greater than 150 °A.

Hung and Wei (1980a) studied the kinetics of hydrodemetallation of nickel etioporphyrin and nickel tetraphenylporphine in a batch autoclave, with white oil as a solvent and CoO_3-MoO_3/Al_2O_3 as catalyst without presulfiding. The effects of hydrogen pressures up to 125 atm. and a temperature between 287 and 357 °C were studied. Up to 90% nickel removal the data can be described by fractional order kinetics. The activation energy is from 27 to 34 kcal/gmol, and the pressure dependence on hydrogen is from 1.5 to 2.2 order. There was no diffusion effect. The rates with clean oil and model compounds are atleast 100 times faster than previous work with residual oil and presulfided catalysts.

Hung and Wei (1980b) studied the kinetics of hydrodemetallation of vanadyl etioporphyrin in a batch autoclave, with white oil as a solvent and CoO_3-MoO_3/Al_2O_3 as catalyst without presulfiding. The results showed that up to 90% vanadium removal the data can be described by fractional order kinetics. In comparision to nickel removal, vanadium removal has a larger activation energy and a smaller hydrogen pressure dependence. A few runs

with mixed vanadyl and nickel etioporphyrins showed that while the presence of vanadyl compounds will supress the nickel removal reaction, the reverse suppression is less significant.

Tamm et al. (1981) studied the effects of feed metals on catalyst aging in hydroprocessing residuum. Electron microprobe techniques were used to study the deposition of nickel, vanadium and iron compounds on and in the catalyst during hydroprocessing of residuum. Both the distributions of the deposited metals and the effects of process and catalyst variables on those distributions indicate that removal of nickel and vanadium is diffusion controlled and removal of iron is reaction controlled. The metals concentration at the point of maximum deposit (catalyst near the reactor inlet) reaches a limiting value before the catalyst bed is fully deactivated.

2.6 Hydroprocessing Catalysts:

Hydroprocessing catalysts, in their initial state, are composed of transition metal oxides dispersed on a high surface area support, which is almost always γ-Al_2O_3. They typically contain 2-5 wt% NiO (or CoO) and 12-20 wt% MoO_3 (or WO_3). The presence of Mo (or W) is essential to the activity of the catalyst; and Ni (or Co), having

little activity alone, acts as a promoter.

By successive impregnation or coprecipitation, the metal oxides are deposited on the support and then calcined (Gates et al. 1979). As a result of pretreatment of the catalyst in a stream of hydrogen sulfide and hydrogen, or through proprietary sulfiding techniques, the metal oxides are partially or completely converted to metal sulfides. Smaller amounts of oxysulfides, polymeric sulfur, Mo(V) and Mo(VI) may also be present. The interaction of MoS_2 with support is weaker than that of MoO_3 with support.

Sulfided $CoO-MoO_3/\ \gamma-Al_2O_3$ is the preferred choice for hydrodesulfurization; sulfided $NiO-MoO_3/\ \gamma-Al_2O_3$ and sulfided $NiO-WO_3/\ \gamma-Al_2O_3$ is frequently the choice for hydrodenitrogenation. Gates et al. (1978) showed that sulfided $NiMo/Al_2O_3$ catalyst is twice as active as $CoMo/Al_2O_3$ for hydrogenation. Sulfided $NiO-WO_3/SiO_2-Al_2O_3$ (the support is acidic) is a preferred catalyst for hydrocracking. All of these catalysts catalyze all the above mentioned hydroprocessing reactions, but the selectivity different reactions varies from one to the other, selectivity being higher for the reactions, for which they are preferred (Ahuja et al., 1970).

$NiMo/Al_2O_3$ and other hydroprocessing catalysts are

extremely complex and their charecterization is a subject of active research. Much research has been carried out on the structure of hydrotreating catalysts, particularily of $CoMo/Al_2O_3$. Techniques such as X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), electron spin resonance (ESR), infrared spectroscopy (IR) and edge X-ray absorption fine structure (EXAFS) have been used to study the structure of molybdenum and cobalt on the catalyst surface, the role of promoter cobalt, and the interaction of cobalt and molybdenum with alumina support.

The catalytic sites on hydroprocessing catalyst have been suggested from various surface investigations and kinetic results. Electron Spin Resonance (ESR) studies of sufided Mo/Al_2O_3 and $NiMo/Al_2O_3$ suggested the existence of surface anion vacancies on these catalysts. Voorhoeve and Stuiver (1971b) related benzene hydrogenation and the ESR intensities of W ions in a series of sulfided NiW/Al_2O_3 catalysts. The good correlation between them suggested that hydrogenation reaction occurs on surface anion vacancies which are formed by the loss of sulfur from WS_2 structure.

It is often assumed that hydrogen and the heteroatom compounds adsorb on different catalyst sites. On sulfided catalysts, hydrogen is believed to adsorbed dissociatively on sulfur atoms, forming hydrosulfide groups (Weisser and

Landa, 1973; Massoth, 1975)

Desikan and Amberg (1964) studied the poisoning effect of pyridine on thiophene HDS, and suggested two kinds of catalytic sites on $CoMo/Al_2O_3$. Site I is responsible for olefin hydrogenation and thiophene HDS, and has strong affinity for thiophene and pyridine. Site II is weak electrophilic and facilitates hydrogenolysis of hydrothiophenes.

Later Satterfield et al. (1975) also proposed two types of catalytic sites on $CoMo/Al_2O_3$ in their work of simultaneous HDS/HDN reactions. Site I is active for HDS reaction and sensitive to nitrogen base; site II is much less active for HDS, and less susceptible to pyridine poisoning.

The involvement of the support in the hydroprocessing reactions is another subject not fully understood. Ahuja et al. (1970) reported a study involving the effect of promoters and supports on hydrogenation, hydrode sulfurization and isomerization reactions. A few of the important results pertaining to supports and promoters are presented in what follows.

Different constituents in the hydroprocessing catalysts seem to have considerably different effects on the hydrogenation activity of the catalyst. Catalysts

containing tungsten sulfide show far better benzene hydrogenation activity than those containing molybdenum sulfide, and for both types nickel is a better promoter.

The greatest hydrogenation activity (for benzene and toluene hydrogenation) for all the promoted catalysts occurs at about the Group VIII metal/Group VI A metal ratio of about 0.3. The total sulfur content of the catalyst passes through a maximum at about the same ratio; the connection between the two is not yet understood.

The active sites present in the bulk and supported catalysts are presumably the same; the carrier does not affect the intrinsic activity for aromatic hydrogenation, but increases the total number of sites due to dispersion (Ahuja et al., 1970; Voorhoeve and Stuiver, 1971b).

On supported promoted catalysts, most of the isomerization activity is due to support. Acidic supports, like silica-alumina, show much higher isomerization activity than silica or alumina supports. Addition of even small quantities of basic reagents like ammonia or pyridine almost entirely eliminates the isomerization activity (Ahuja et al., 1970).

The mechanisms of aromatic hydrogenation reactions are not well understood. For symmetrical molecules such as benzene, the first adsorption of the aromatic might be

envisaged as forming a flat or "half sandwich" species parallel to the surface and located above Mo cations. The anion vacancy necessary to allow formation of such a species might be too small to accomodate larger aromatic molecules. These might be then adsorbed on edge, perpendicular to the surface, or flat in positions where enough room could be made by removal of more contiguous sulfur atoms, as a result from, say, application of higher hydrogen partial pressures (Gates et al., 1979).

Chapter III

EQUIPMENT AND PROCEDURES

For the experimental investigation of the effects of hydrogen sulfide, ammonia and water on hydrogenation of propylbenzene, reactions were carried out in a batch autoclave reactor. Under high hydrogen pressures, these components were contained in hexadecane in contact with commercial $NiMo/Al_2O_3$ catalyst. This chapter describes the equipment and materials used to achieve the goal. Analytical methods and experimental procedures are also detailed.

3.1 Reactor System:

In this section the design and operation of the batch slurry reactor is explained. A schematic of the reactor system is shown in Figure 3.1.1.

A standard one-liter autoclave (Autoclave Engineers Inc., Erie, PA, USA) equipped with disperse-mix MagneDrive II agitator was used for the reaction studies. However, some modifications were made to suit the requirements. A porous stainless steel filter was welded at the end of hydrogen inlet line inside the autoclave to disperse the hydrogen in fine bubbles. Another porous stainless steel filter was welded at the end of liquid sampling line

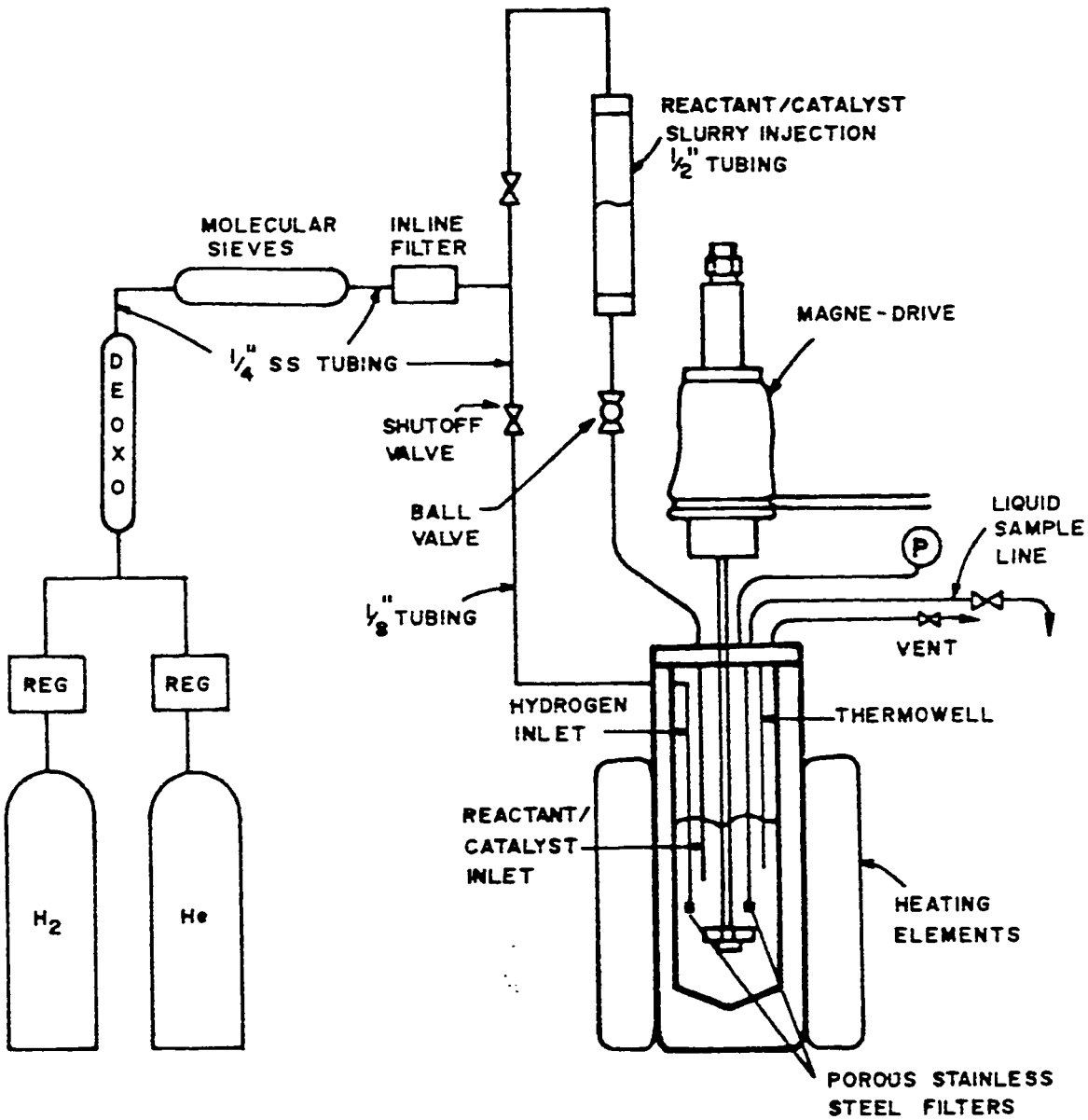
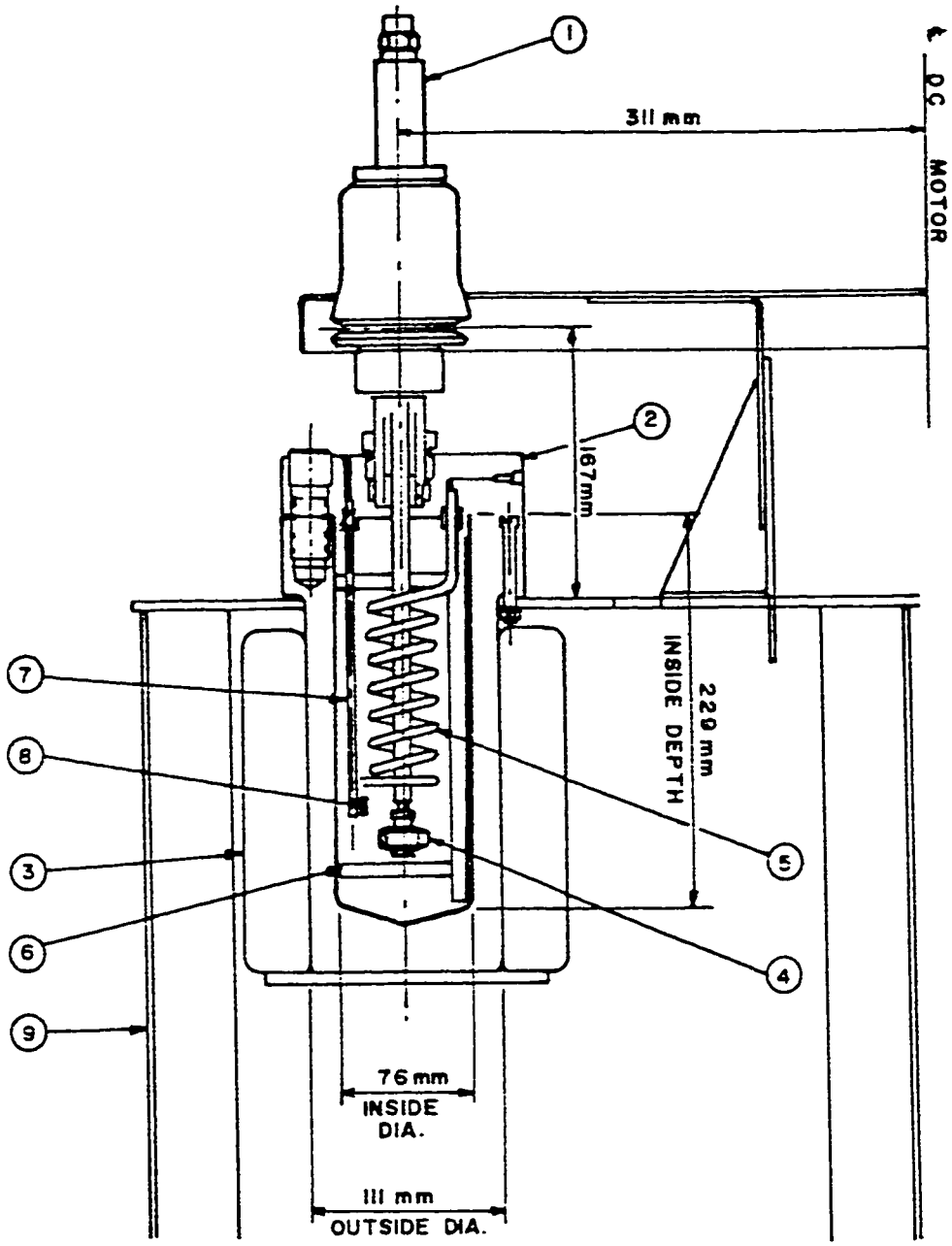


FIGURE - 3.1.1 DIAGRAM OF EXPERIMENTAL SET-UP



1. MAGNE-DRIVE
2. COVER
3. FURNACE
4. 1/4" DIA. IMPELLER
5. COOLING COIL
6. BAFFLE
7. THERMOWELL
8. SAMPLE TUBE
9. STAND

FIGURE - 3.1.2 DETAILS OF AUTOCLAVE

inside the autoclave to filter out the catalyst particles. Thus, only liquid samples were removed and the amount of catalyst remained constant throughout the experiment. The details of the autoclave are shown in Figure 3.1.2.

A special injection system was designed and used to inject a slurry of catalyst and reactants in a small amount of carrier liquid (hexadecane) into the reactor after it has been stabilized at reaction temperature. This technique allows the precise definition of zero-time. Also, this eliminates the complications involving possible catalyst activity changes and reactions during long heat-up periods. Such complications would have prevented the elucidation of isothermal kinetics from the conversion data. The catalyst injection tubing was located above the autoclave and was separated from the reactor by a ball valve.

MangeDrive II is a high-speed rotary agitator driven by a DC motor. The ImPak Plus D-C V*S drive controller (Reliance Electric Co., Cleveland, Ohio, USA) was used to vary the motor speed. An Analog Tachometer indicates the inner shaft speed upto a maximum of 2500 rpm. The desired rpm can thus be achieved by monitoring the speed control switch. To avoid overheating of MagneDrive, water is continuously passed through the ports provided for the purpose.

The stirring is done by turbine-type agitator (Disperimax) provided with a hollow shaft in conjunction with removable baffles in the vessel. When in operation, a low pressure area is created at the turbine impeller. The gases are drawn down through the hollow shaft and dispersed in the liquid. The bubbles are broken up by the baffle provided. This type of agitation provides solid suspension and insures constant circulation of reactant gases through the liquid.

A jacket-type heater is furnished as standard equipment with the autoclave. The furnace has resistance windings and insulation enclosed in a sleeve-type jacket which slides onto the body of the autoclave. The maximum allowable temperature for the furnace elements is 760 °C. If rated voltage were applied continuously, this limit may exceed and the furnace elements may burn out. To avoid this, the furnace element temperature is regulated by a solid state temperature control system FURNATOL I (SYBRON Thermolyne, Dubuque, Iowa, USA). The reactor temperature is measured by placing a Chromel-Alumel Type 'K' thermocouple in the thermowell immersed in the reaction mixture. A digital temperature indicator (DIGITRON Instrumentation Ltd., Model 3750-K) reads the reactor temperature monitored by the thermocouple. Since element temperature will be considerably higher than reactor temperature, a higher temperature setting is required at

the temperature controller than the desired reactor temperature. A coil is provided for passing water, if cooling is needed.

The maximum allowable pressure of the reactor system is 6000 psig. The pressure in the gas cylinders is utilized to attain the operating pressures. Thus operating pressures are limited by the supply pressures (usually 2000 psig.) of gas cylinders. The pressure is adjusted by regulator (Matheson International, East Rutherford, NJ, USA) at the cylinder outlet. The standard pressure guage of 3-1/2 " dial guage with a 403 SS Bourdon tube indicates the pressure in the reactor.

To ensure safety, a 1/8 in. steel barricade was built to surround the autoclave, connection tubings and fittings etc. Only the control valves, switches and indicators (for temperature, pressure and stirrer speed) were outside so that the operation of the system can be controlled safely from outside. The vent from the reactor is directly connected to ventilation hood to allow gases to escape. A H_2S gas monitor (Texas Analytical Controls, Inc., Houston, TX, USA) was installed to detect any leak of poisonous H_2S. The material of construction of autoclave autoclave is 316 stainless steel. The connection tubings (1/8 in. and 1/4 in.), fittings and valves are all made up of stainless steel. This was

Table 3.1.1

OPERATING CONDITIONS OF AUTOCLAVE REACTOR

Temperature:	330, 350 or 375 °C
Total pressure:	1000 psig.
Catalyst:	$NiMo/Al_2O_3$ (either in oxide or in sulfided form)
Catalyst loading:	2 wt% (8gms. per batch)
Carrier oil:	n-Hexadecane (500 cc per batch in 1-L autoclave)
PBz loading:	1 wt% (6.4×10^{-8} gmol/lit)
Partial pressure of H_2S, NH_3 and H_2O:	100 mmHg each (whenever needed)
Stirrer speed:	1500 rpm

necessary to prevent corrosion by CS_2 and H_2S.

Gas cylinders were kept just outside the barricade. The gases were passed through a DEOXO unit (Engelhard Industries Division, Union, NJ, USA; Model D-25-2300) for removing any oxygen from the gases. In series with this were a dehydration column (containing Type 13X molecular sieves) and an inline filter to remove traces of moisture and dust particles, respectively. The gases were then introduced into the reactor through a valve and the porous stainless steel filter.

The operating conditions are summarized in Table 3.1.1. The experimental procedure consists in loading the cleaned reactor with about 480-485 cc of hexadecane. The reactor cover is then closed by eight screws. A slurry of catalyst and reactant compound (Propylbenzene) in hexadecane was taken in the catalyst injection tubing in required quantities. For the runs with hydrogen sulfide, ammonia and water, the compounds generating them is also taken in the catalyst injection tubing. While loading sulfided catalyst, care was taken to minimize contacting with air. Normally, the reactor contained 480-485 cc and the injection tubing contained 15-20 cc of hexadecane.

The reactor was pressurized to about 100 psi with helium and then depressurized; the procedure was repeated several times, to ensure complete removal of oxygen from

the reactor system. The reactor was pressure tested at the intending operating pressure (1000 psig). Finally, the reactor is pressurized to 500 psi with hydrogen and heating is started.

When the temperature is stablized, the slurry was injected into the autoclave using hydrogen pressure. As soon as the cold slurry is injected, the temperature in the autoclave dropped about 15 °C below the initially stablized temperature. But it restablized to the desired temperature within 5 minutes. During the operation the temperature was controlled within ±2 °C. The pressure in the autoclave was maintained at the desired level (1000 psig) by adding small amounts of hydrogen, as needed during the course of the reaction.

A stirrer speed of 1500 rpm was maintained during all the experiments of the present study. Previous studies of hydroprocessing reactions carried out using similar reactor (Rieff, 1977; Shih et al., 1977; Bhinde, 1979; Krishnamurthy et al., 1979; Sapre and Gates, 1981) had shown that external mass transfer resistances were insignificant at this stirrer speed.

Periodically, liquid-phase samples were taken out from the reactor through the porous stainless steel filter and the sampling valve. The liquid in the sampling line (about 3 cc) was always rejected prior to sampling to

enable the collection of authentic samples from the reactor. The change in the volume of the liquid in the reactor during an experiment was typically less than 10%. The samples were analyzed by Gas Chromatography. The analytical methods are described in Section 3.3.

3.2 Catalyst and Chemicals

The commercial hydrotreating catalyst used in all the experiments was NiMo/ γ-Al_2O_3 (AERO HDS-3; American Cyanamid Co., Wayne, NJ, USA). The physical properties and chemical composition of this catalyst are given in Table 3.2.1. The catalyst was supplied in oxide form as 1/8 in. extrudates. It was crushed and sieved before use. Only the particles that pass through 170 mesh (sieve opening: 0.088 mm) but not through 200 mesh(sieve opening: 0.074 mm) were used. Such a size was required to have negligible internal mass transfer resistances in the system.

The catalyst was used in either oxide form or after sulfiding it in the laboratory. There are many sulfiding procedures given in literature. The one used in this work is described here. The catalyst required for each run (about 8 gms.) was taken in a 1/2 in. stainless steel tube so as to make a catalyst bed. This was kept in an oven and connected to the gas supply lines. The catalyst bed

Table 3.2.1

Typical Properties of American Cyanamid AERO HDS-3A $NiMo/Al_2O_3$ Catalyst

Chemical Composition (wt%, dry basis)	
Molybdenum (MoO_3)	15.4
Nickel (NiO)	3.2
Sodium (Na_2O)	0.03
Iron (Fe)	0.03
Sulfate (SO_4)	0.3
Silicondioxide (SiO_2)	0.1
Loss on ignition at 900 °F, wt%	1.2
Physical Properties	
Surface area, sqm/gm	200
Pore volume, cc/gm	0.60
Compacted bulk density, lb/cft	45
Crush strength, lb/mm	3.4
Loss on abrasion, wt%	0.4

Supplied by the manufacturer (American Cyanamid Co., Wayne, NJ, USA)

was heated to 325 °C while helium is flowing through it at a rate of 100 cc/min. When the temperature of 325 °C is reached, helium flow is cut off and the flow of 10% H_2S in H_2 was started. The amount of H_2S passed over the catalyst was such that the catalyst saw atleast 10 times the stoichometric amount of sulfur necessary for complete conversion of metal oxides to metal sulfides. At a flow rate of 100 cc/min, it requires 8 hours for 8 grams of catalyst. After 8 hours, the flow of H_2S/H_2 gas mixture was cut off and helium is passed over the hot catalyst. The oven is shut off and cooling starts. Flow of helium is continued until the catalyst is cooled down completely and is required for the use. To avoid reoxidation by air, the sulfided catalyst was immediately slurried with a small amount of carrier oil and taken in the injection tubing.

In model compound studies, the respective compound is dissolved in an inert carrier liquid. The most common and inexpensive carrier liquid is a white oil (Nujol), but this may contain hundreds of different molecules of naphthenes, parrafins and isoparrafins. Since in a typical study the product contsists of less than 1% of various compounds, the use of white oil would make the Gas Chromatographic analysis with conventional detectors extremely difficult. Hence a single component liquid carrier such as n-hexadecane (paraffins heavier than n-

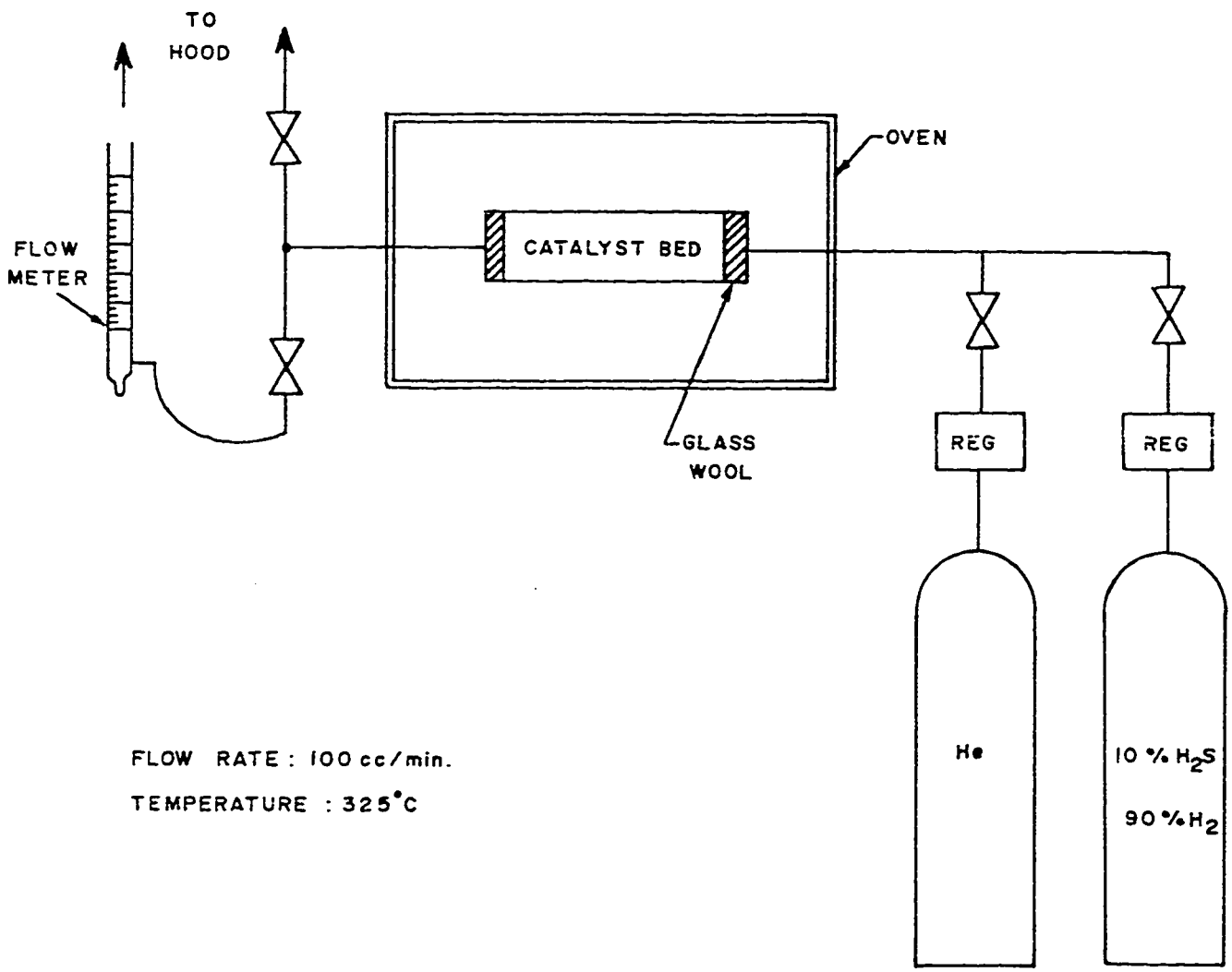


Figure 3.1.3 Experimental set-up for catalyst sulfiding

hexadecane are solids at room temperature) is desirable (Yang, 1982). For this reason, n-hexadecane was used as a carrier liquid. Typical properties of n-hexadecane are given in Table 3.2.3. The olefin-free n-hexadecane was obtained from Fluka AG (West Germany) and from Humphrey Chemical Co. (North Haven, CT, USA).

The model aromatic hydrocarbon used was propyl benzene. Propylbenzene was selected because it and propylcyclohexane are the princpal products formed by HDN of quinoline, a model compound which was studied extensively. About lwt% of propylbenzene was taken in hexadecane. Typical properties of propylbenzene are given in Table 3.2.3. Propylbenzene was purchased from Fluka AG (West Germany).

The hydrogen used is of ultra-high purity of 99.99%. Helium was 99.98% pure. Both of these gases were purchased from Saudi Industrial Gas Co., (Alkhobar, KSA). The 10% H_2S/H_2 gas mixture needed for catalyst sulfiding was obtained from Matheson International (East Rutherford, NJ, USA).

For the runs in which hydrogen sulfide was present, it was generated, in situ, by adding carbondisulfide to the reaction mixture. The addition of carbondisulfide had been a popular choice in several related hydroprocessing studies (Voorhoeve and Stuiver, 1971; Gultekin, 1980;

Table 3.2.3

Properties of Propylbenzene and Hexadecane

	Propylbenzene*	Hexadecane**
Molecular Weight	120.2	226.5
Specific Gravity	0.862	0.774
Melting Point, °C	-99.5	18.5
Boiling Point, °C	159.2	287.5

Sources:

*Dean, 1973
**Perry and Chilton, 1974

Sapre and Gates, 1981; Gultekin et al., 1984). The carbondisulfide was almost instantaneously and completely converted into hydrogen sulfide under the reaction conditions. The rate of the hydrogenolysis reaction

$$CS_2 + 4H_2 \longrightarrow 2H_2S + CH_4$$

was atleast three orders of magnitude greater than that of the benzene hydrogenation (Voorhoeve and Stuiver, 1971a). Therefore, it would not interfere with the hydrogenation studies. A hydrogen sulfide partial pressure of about 100 mmHg was maintained.

Similarily, for the runs in which ammonia was present, it was generated, in situ, by adding diaminoethane to the reaction mixture. Primary amines rapidly hydrogenated to ammonia under the reaction conditions (Goudriaan,1974; Sonnemans and Mars, 1974; Gultekin et al, 1984) Water is added for the runs in which it was needed. To study the combined effects, these compounds are simultaneously added to the reaction mixture.

3.3 Analytical Methods

Liquid samples were analyzed by Gas-Liquid Chromatography. A sophisticated VARIAN Model 3700 Gas Chromatograph (Varian Instrument Group, Walnut Creek, CA, USA) was used for the purpose. The GC is equipped with a

nitrogen-specific detector and a thermal conductivity detector. However, only the later was used for this work. Other features of the GC are Electro Sensor Panel (ESP) monitor which continuously checks operating parameters and Automatic Linear Temperature Programmer (ALTP) for easier and accurate column temperature progamming.

The GC is hooked to a highly sophisticated microprocessor-controlled VISTA 402 Chromatography Data System which is capable of controlling upto four GCs while simultaneously calculating and reporting the data. The interactive CRT for easier monitoring and controlling and the advanced printer/plotter which gives annotated analysis report are the unique features of VISTA 402.

For the analysis of reaction products, the choice of column was the most difficult one. When oxide form of catalyst was used some of the hexadecane cracked. One of the cracked products was eluting almost at athe same time as propylbenzene. Similarily, another one was eluting along with propylcyclohexne. This complictes the resolution and identification of compounds. The column which resolved all the reaction products in a reasonable retention time was a 2m. long high polarity 15% FFAP on 80/100 mesh Chromosorb W packed in a 1/8 in. stainless steel tubing. Other columns tried were 2m. long 10% OV-101 on 80/100 mesh Chromosorb W and 2m. long 10%

Carbowax 20M on 80/100 mesh Chromosorb W-HP. Many combinations of column, injector and detector temperatures and carrier gas (helium) flow rates were tried. Column oven temperature promming was also tried. Based on these trials, a programmed column temperature of 50 °C to 180 °C at 3 °C/min and a helium flow rate of 25 cc/min were found to be the most satisfactory. The final set of operating parameters are listed in Table 3.3.1. Sample Chromatograph and analysis report as obtained from the VISTA 402 are shown in Figure 3.3.1. The analysis time for one sample was about 36 minutes.

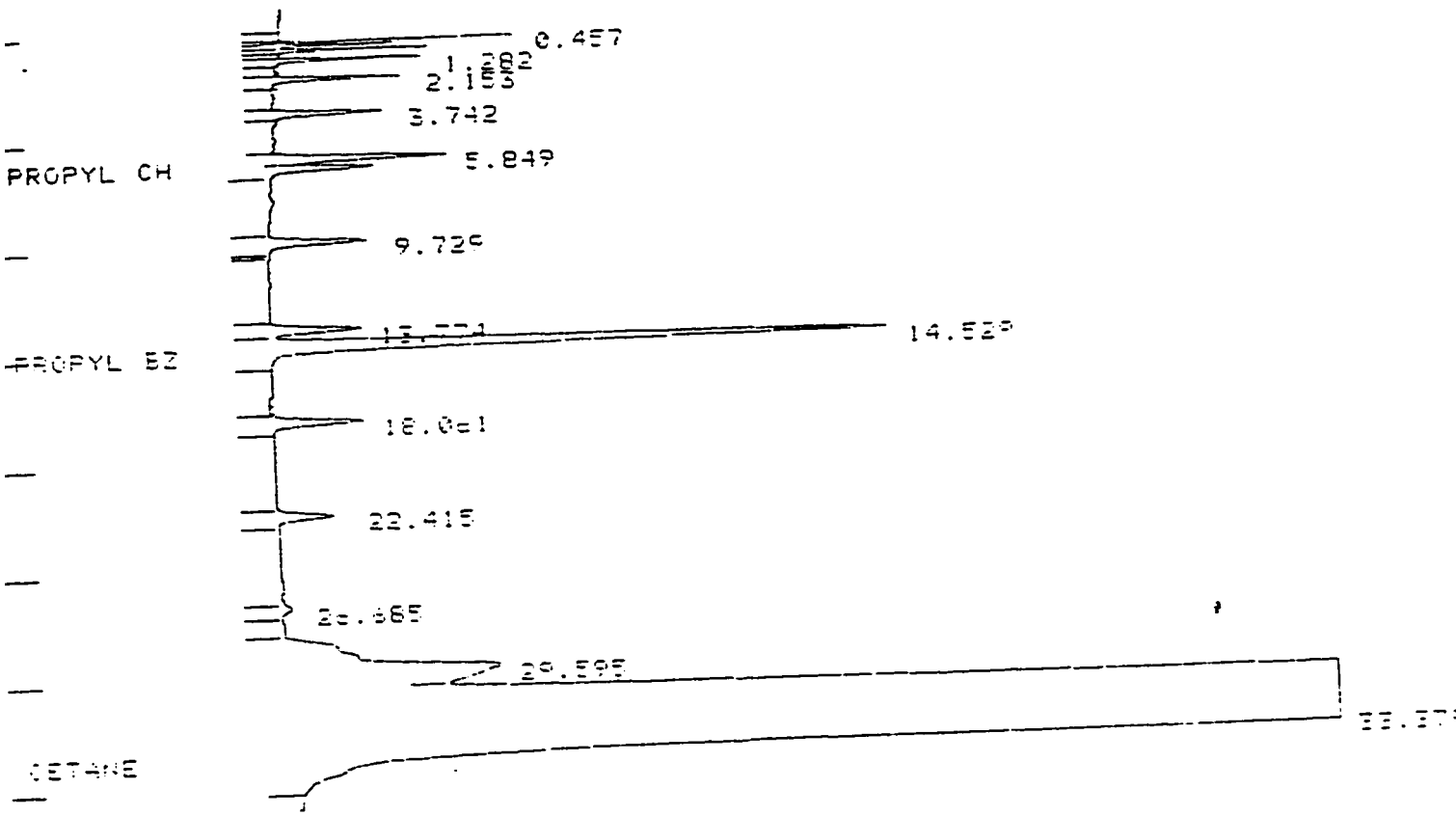
Propylbenzene and propylcyclohexane were identified by their retention times at the above stated GC condtions. Although pure propylcyclohexane was not available, but since it was the only product of propylbenzene hydrogenation, its identification was easy. The retention time propylbenzene hydrogenation was 14.5 minutes while propylcyclohexane elutes after 5.8 minutes. Elution of hexadecane requires higher column temperature and hence its retention time is 33.4 minutes.

The response of thermal conductivity detector is given as area counts by the VISTA 402 analysis report. The response of standard samples was determined. The standard samples contained 0.3 wt% to 1 wt% propylbenzene dissloved in hexadecane. Within this range of concentration, the

Table 3.3.1

Gas Chromatograph Operating Conditions for the Analysis of Propylbenzene Hydrogenation Products

Gas Chromatograph	VARIAN Model 3700
Detector	Thermal Conductivity
Column	2m long 15% FFAP on 80/100 mesh Chromosorb W packed in a 1/8 in SS tubing
Column Temperature	50 °C to 180 °C at 3 °C/min
Carrier Gas	Helium at 25 cc/min
Injector Temperature	200 °C
Detector Temperature	220 °C
Filament Temperature	280 °C
Sample Size	1 microliter

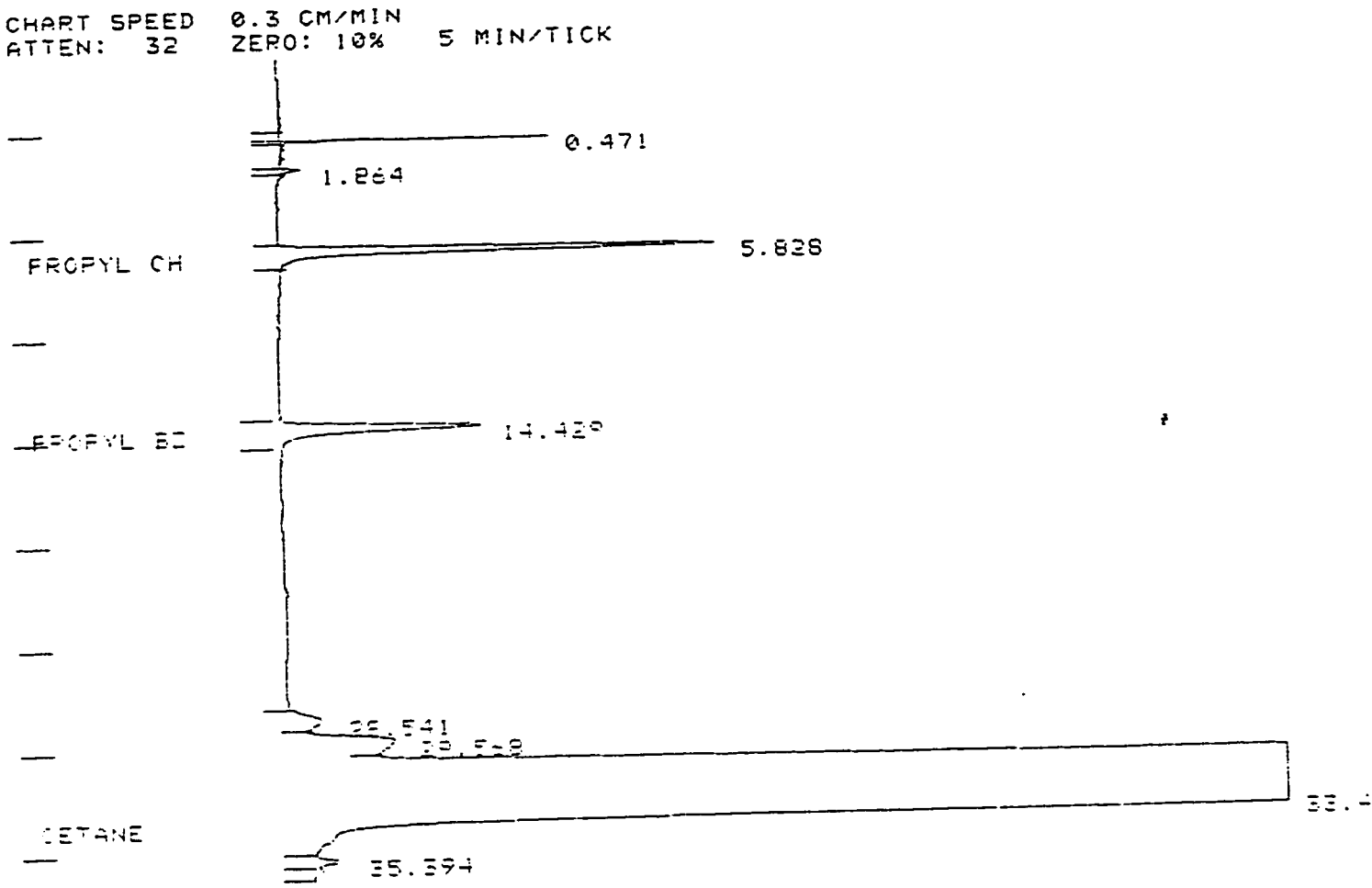


TITLE: 350 C. 1000 PSIG. PEZ 20:37 25 JAN 94

CHANNEL NO: 1 SAMPLE: TIME 9 HRS. METHOD: S44

PEAK NO	PEAK NAME	RESULT AREA %	TIME (MIN)	AREA COUNTS	SEP CODE
1		0.0462	1.282	22435	BB
2		0.0577	2.155	28031	BB
3		0.0657	3.742	31891	BB
4	PROPYL CH	0.1433	5.849	69567	BV
5		0.0805	9.279	39084	VB
6		0.0868	9.726	42170	BB
7		0.0893	13.774	43361	BV
8	PROPYL BZ	0.6826	14.529	331443	VB
9		0.0916	18.061	44492	BB
10		0.0585	22.415	28392	BB
11		0.8678	20.595	421380	BV
12	CETANE	97.7300	35.379	47454200	VB
TOTALS:		100.0000		48556500	

Figure 3.3.1 Sample Chromatograph for Products of PBz Hydrogenation on Oxide NiMo/Al_2O_3 Catalyst



TITLE: 330 C, 1000 PSIG, PBZ + H2S 14:48 23 FEB 84

CHANNEL NO: 1 SAMPLE: TIME 2.0 HRS METHOD: SAM

PEAK NO	PEAK NAME	RESULT AREA %	TIME (MIN)	AREA COUNTS	SEP CODE
1		0.0290	0.471	15219	BB
2	PROPYL CH	0.3915	5.828	205369	BB
3	PROPYL BZ	0.2483	14.429	130239	BB
4		0.0709	28.541	37183	BV
5		0.3082	29.568	161675	VV
6	CETANE	98.9281	33.413	51894700	VV
7		0.0241	35.394	12623	T
TOTALS:		100.0000		52457000	

Figure 3.3.2 Sample Chromatograph for Products of PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst

thermal conductivity detector responds linearly (See Appendix A for details). A sample of one microliter was injected at all times. The area counts of propylbenzene from chromatograms of samples were converted to concentration units by using this response factor. Sample calculations of the conversion based on disappearance of propylbenzene are given in Appendix B.

Chapter IV

RESULTS AND DISCUSSIONS

In this chapter, results of experiments are presented and discussed. The experiments were designed to study the effects of hydrogen sulfide, ammonia and water on the catalytic hydrogenation of propylbenzene. The experiments were carried out in an one-liter batch slurry reactor (as described in the previous chapter), in the presence of commercial $NiMo/Al_2O_3$ catalyst; either in oxide form or in sulfided form.

4.1 Results:

The results are presented in the following sequence: First, the results of the preliminary experiments used in the selection of operating conditions are detailed, and then the results of the main experiments with oxide and sulfided forms of catalyst are presented. Finally, the observed effects of the presence of hydrogen sulfide, ammonia and water are reported.

4.1.1 Preliminary Observations:

Preliminary runs were carried out at a total pressure of 500 psig at three temperatures (330, 375 and 420 °C) using 4 gms. of oxide catalyst in 250 cc of hexadecane as carrier liquid. Analysis of products showed that a number of compounds are present; presumably formed due to hydrocracking of hexadecane. At 420 °C (4 gcat/250 cc), the cracking was so severe that more than 50% of hexadecane cracked in about four hours of reaction time. Though cracking of hexadecane should not effect hydrogenation reaction, but the cracking products were making the resolution and identification of compounds (by Gas Chromatography) almost impossible. Another reason for this difficulty was the non-availability of pure propylcyclohexane.

A blank run was also performed with only hexadecane, in the presence of catalyst and hydrogen, in order to differentiate the cracked products from the products of hydrogenation. The analysis of products of this run shows that all the products obtained in earlier runs were products of hexadecane cracking. While no attempts were made to identify these cracking products, they are believed to be shorter-chain paraffins.

These observations lead to the conclusion that more severe conditions, specially higher hydrogen pressures, are required for aromatic hydrogenation over oxide

$NiMo/Al_2O_3$ catalyst. Following run was carried out at 330 °C, but at a hydrogen pressure of 1000 psig. The cracking was much less pronounced at these conditions and hence analysis was relatively easier. Comparision of chromatographs of this run and of blank run shows a distinct peak of propylcyclohexane, the product of propylbenzene hydrogenation.

Based on these observations, the rest of the runs were performed at 1000 psig. An earlier plan of selecting the reaction temperatures of 330, 375 and 420 °C was modified to 330, 350 and 375 °C, also due to above mentioned problem. The runs at 500 psig have to be, unfortunately, discarded.

4.1.2 Hydrogenation of Propylbenzene over Oxidic Catalyst:

It is known that sulfided catalyst is more active than oxide form. However, the reaction mechanism remained unchanged due to sulfiding. Since the reaction is slower with oxide form, one can detect any possible reaction intermediates by using this form of catalyst. Another aim of using this form is to compare its hydrogenation activity with that of sulfided form. This may lead us to some information regarding the catalytic sites, which are not yet fully understood.

Oxide form of commercial $NiMo/Al_2O_3$ catalyst was used for propylbenzene hydrogenation at 330, 350 and 375 °C. The reactant solution contained about 1 wt% of propylbenzene in 500 cc of hexadecane. In all the experiments, 8 gcat was used.

The analysis of products showed propylcyclohexane as the only product of propylbenzene hydrogenation. No other product, such as propylcyclohexene, was observed. Possible dealkylated products, such as benzene or cyclohexane etc., were also not found. This allows the calculation of conversion based on disappearence of propylbenzene.

Percent hydrogenation versus reaction time are plotted for three temperatures in Figure 4.1.1. Summary of data is given in Appendix C.

4.1.3 Hydrogenation of Propylbenzene over Presulfided Catalyst:

Feedstocks always contain sulfur which, under hydroprocessing conditions is removed more readily than nitrogen and oxygen to give hydrogen sulfide. This hydrogen sulfide can partially or completely convert the catalyst to sulfided state. Generally superior performance is obtained by converting the catalyst to the

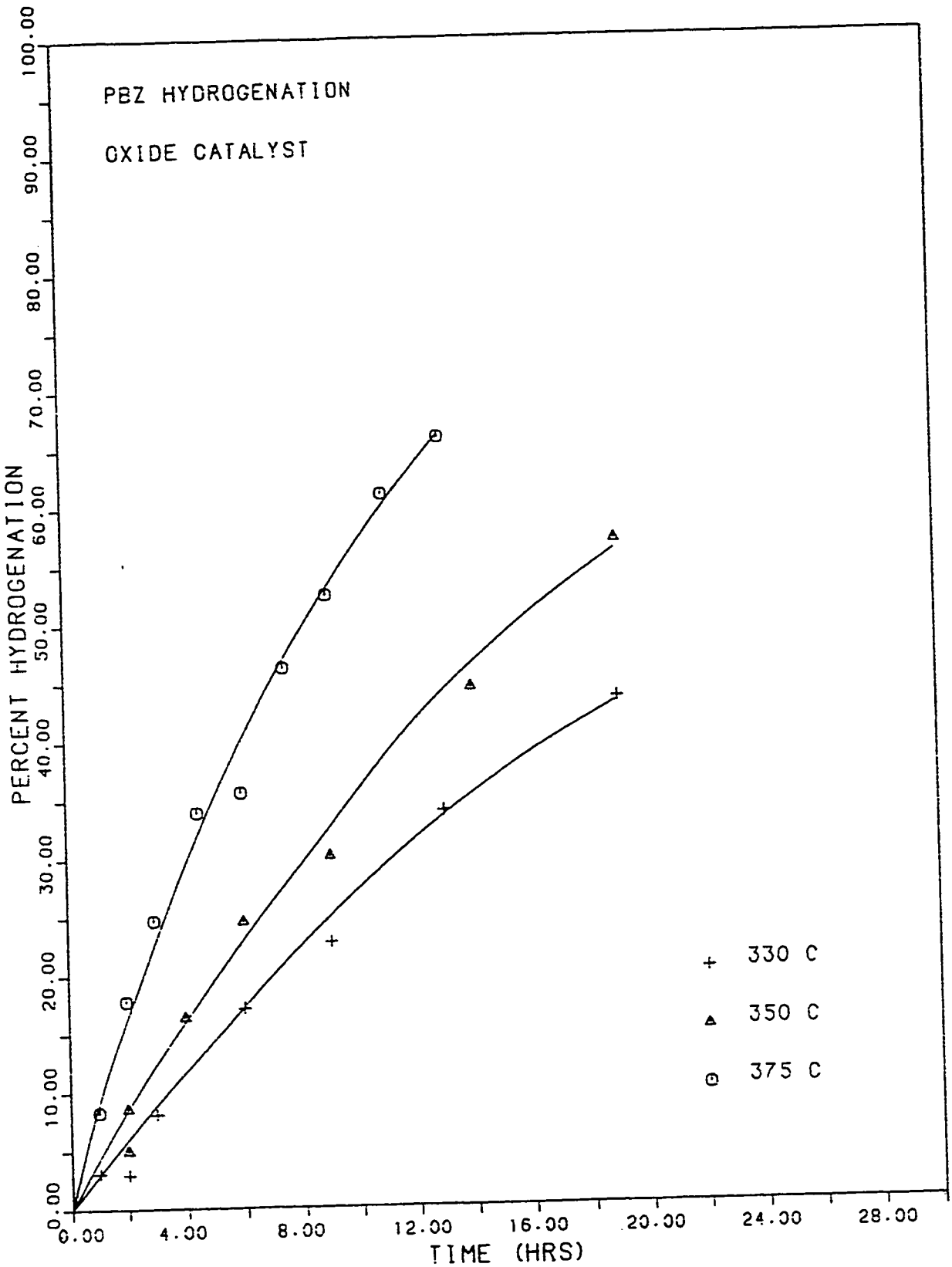


Figure 4.1.1 Percent PBz Hydrogenation on Oxide $NiMo/Al_2O_3$ Catalyst versus Reaction Time

sulfide form under controlled conditions rather than allowing the catalyst to become sulfided by contacting with sulfur-containing compounds in the hydrotreator. Sulfiding of molybdenum-containing catalysts is known to affect their hydrogenation activity. They are more resistant to poisoning by sulfur and to the formation of coke deposits.

In order to increase the relevance of model studies for the practice of hydroprocessing, attention should be paid to both the sulfided state of the catalysts and to the interactions among the compounds actually present in the real hydrotreators.

For this study, sulfiding of the catalyst was done in the laboratory before introducing it into the reactor by passing H_2S/H_2 gas mixture through the catalyst bed at 325 °C (as described in Section 3.2). Sulfided catalyst was used for the rest of the experiments.

Hydrogenation of propylbenzene was carried out at three temperatures of 330, 350 and 375 °C and at a hydrogen pressure of 1000 psig. The reactant solution contained about 1 wt% of propylbenzene in 500 cc of hexadecane.

The analysis of products showed propylcyclohexane as the only product of propylbenzene hydrogenation. No other product, such as propylcyclohexene, was observed.

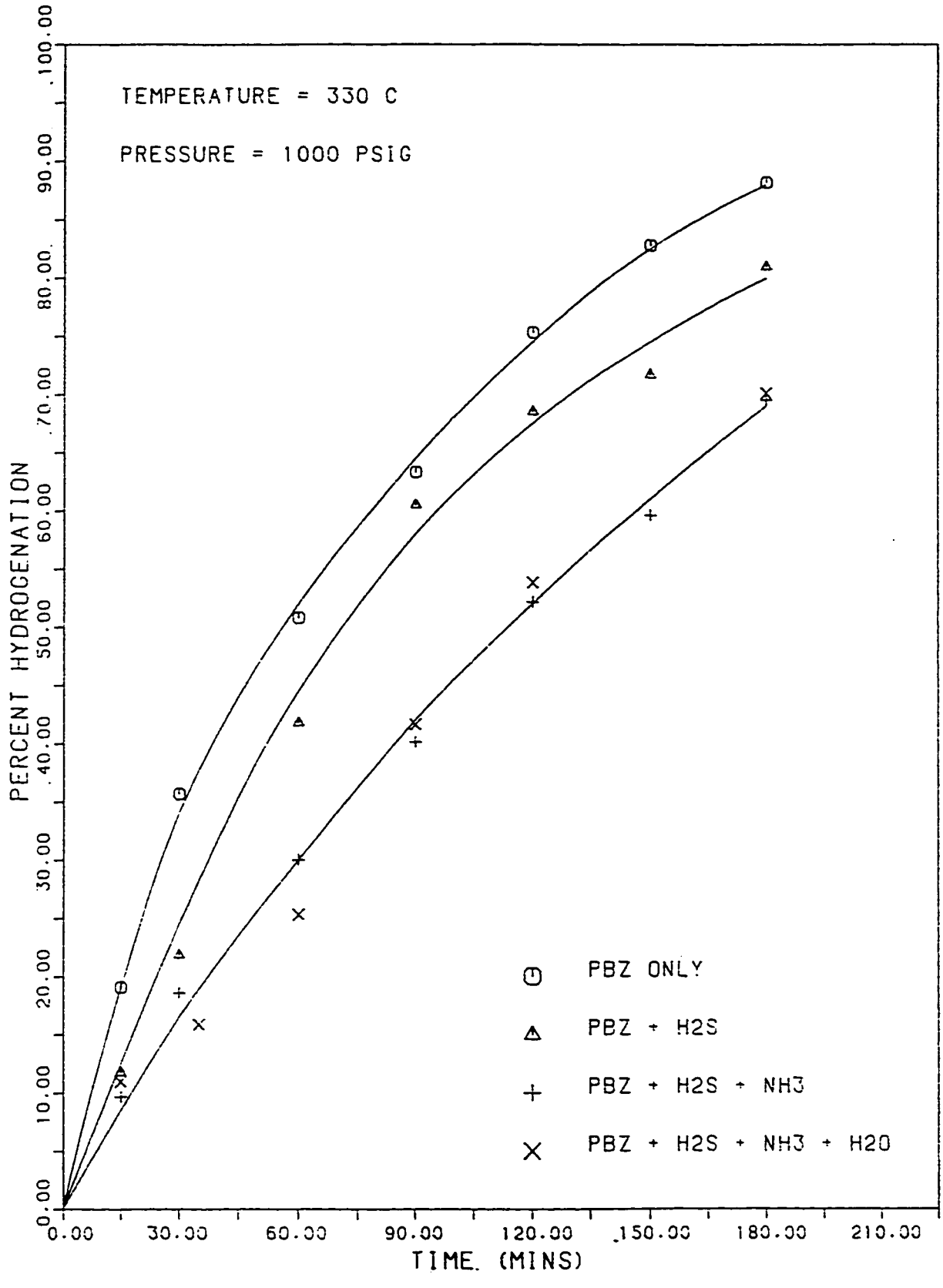


Figure 4.1.2 Percent PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst versus Reaction Time at 330 °C

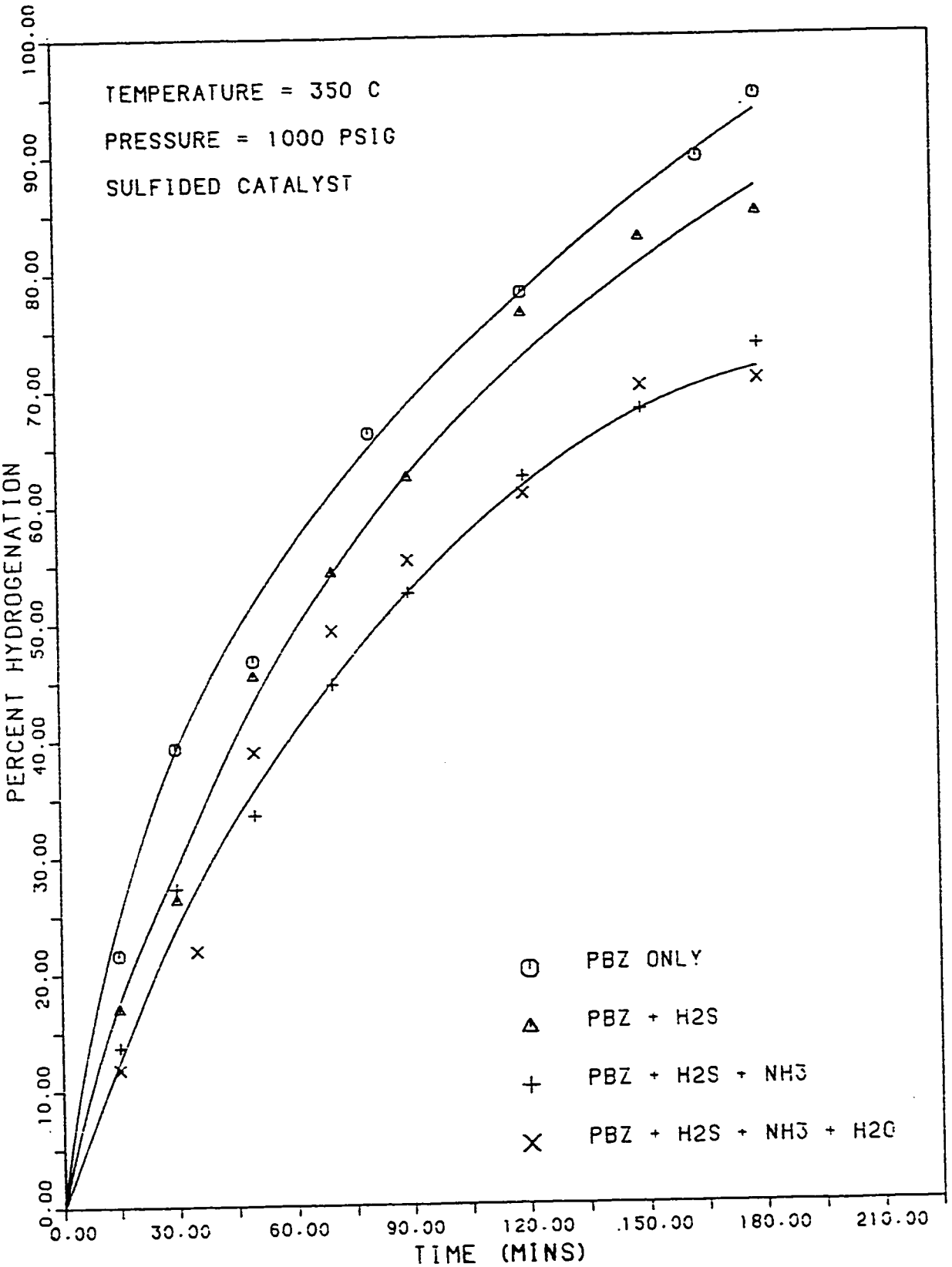


Figure 4.1.3 Percent PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst versus Reaction Time at 350 °C

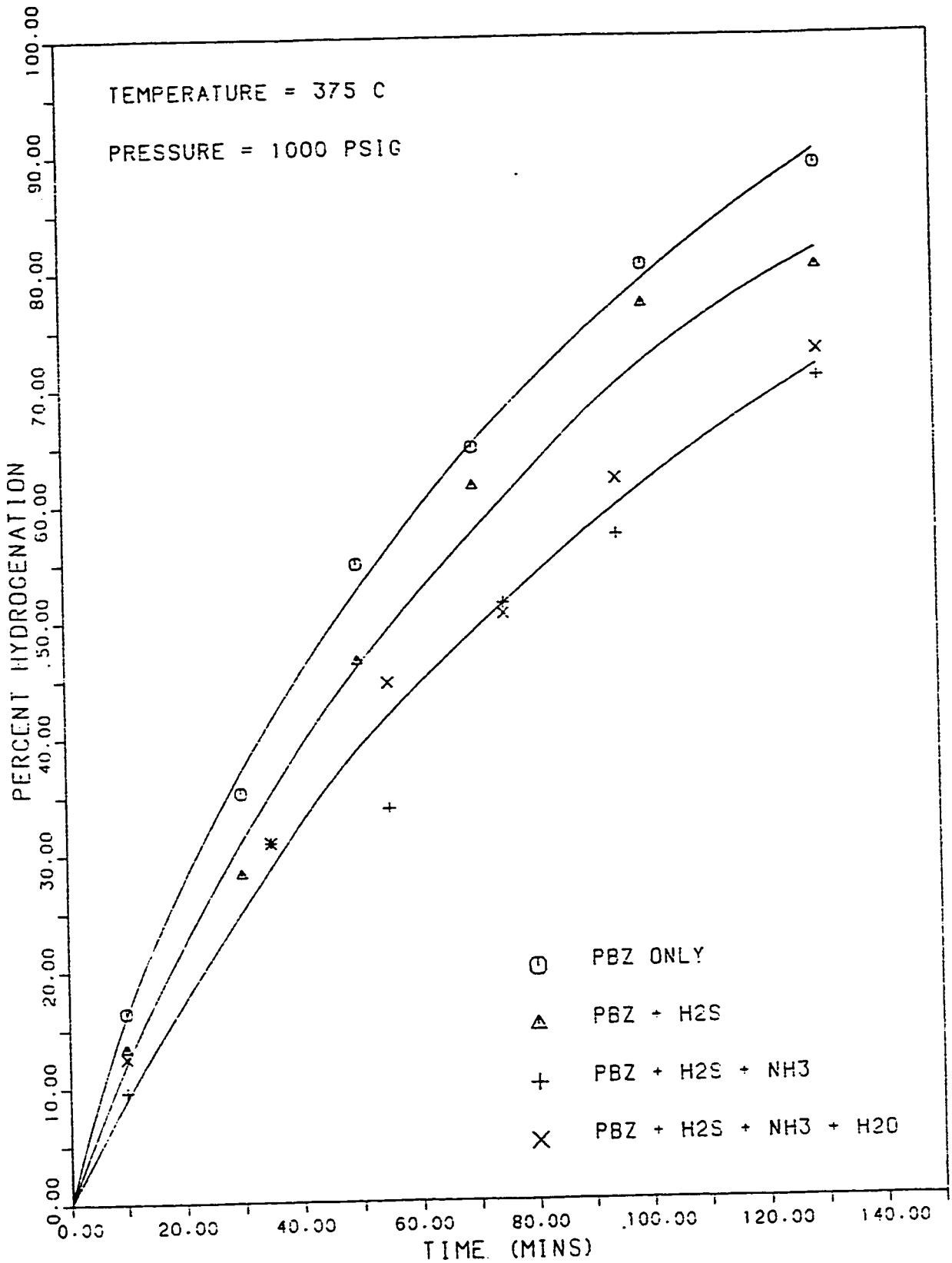


Figure 4.1.4 Percent PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst versus Reaction Time at 375 °C

Possible dealkylated products, such as benzene or cyclohexane etc., were also not found. This allows the calculation of conversion based on disappearence of propylbenzene.

Percent hydrogenation versus reaction time are plotted in Figures 4.1.2, 4.1.3 and 4.1.4 for the runs at 330, 350 and 375 °C, respectively. Each plot shows the curves for hydrogenation of propylbenzene alone, in the presence of hydrogen sulfide and in the presence of hydrogen sulfide and ammonia.

A qualitative comparision between the activity of oxide and sulfided forms of the catalyst can be done by plotting the conversion versus reaction time for both catalysts on the same figure. Such comparisions are shown in Figures 4.1.6, 4.1.7 and 4.1.8 for the temperatures of 330 °C, 350 °C and 375 °C respectively. As is evident from these figures, the effect of sulfiding is to markedly enhance the hydrogenation reaction rate.

Another observation was that with sulfided catalyst cracking of hexadecane was almost zero, in contrast to that with oxide form of catalyst. This observation is explained later (Section 4.2.2)

4.1.4 Effects of Hydrogen Sulfide, Ammonia and Water:

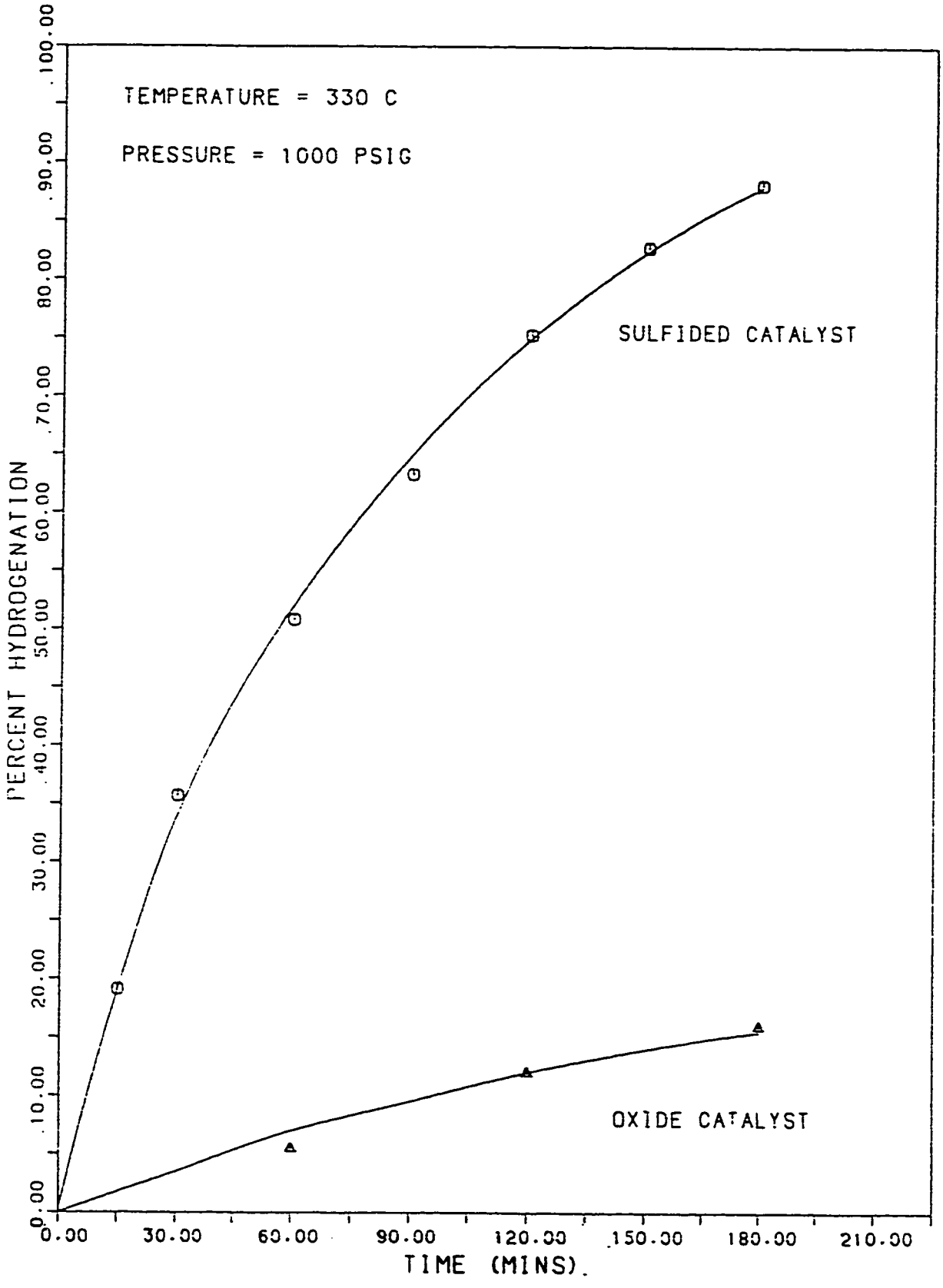


Figure 4.1.5 Comparison of Percent PBz Hydrogenation on Oxide and Sulfided $NiMo/Al_2O_3$ Catalysts at 330 °C

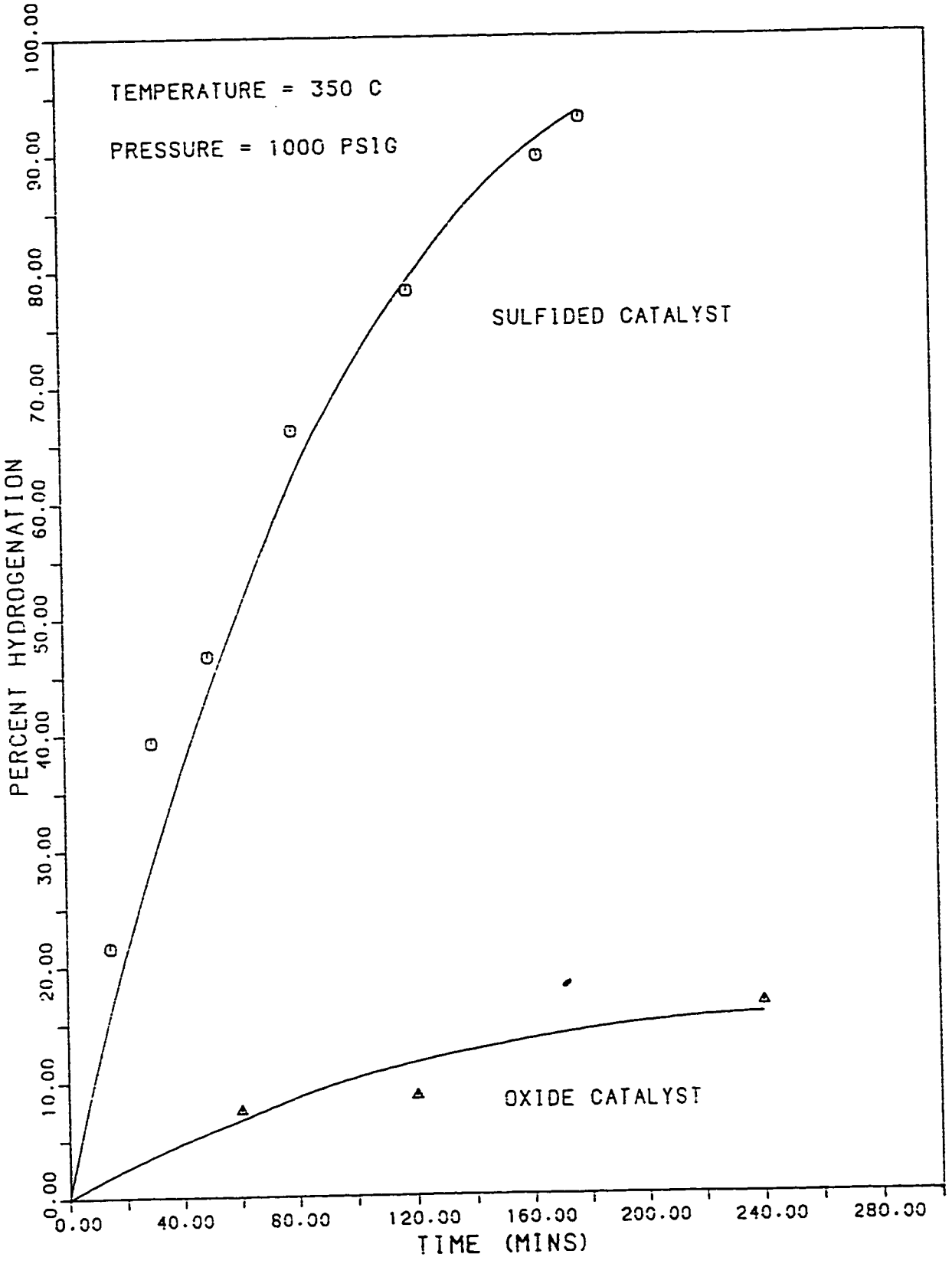


Figure 4.1.6 Comparison of Percent PBz Hydrogenation on Oxide and Sulfided $NiMo/Al_2O_3$ Catalysts at 350 °C

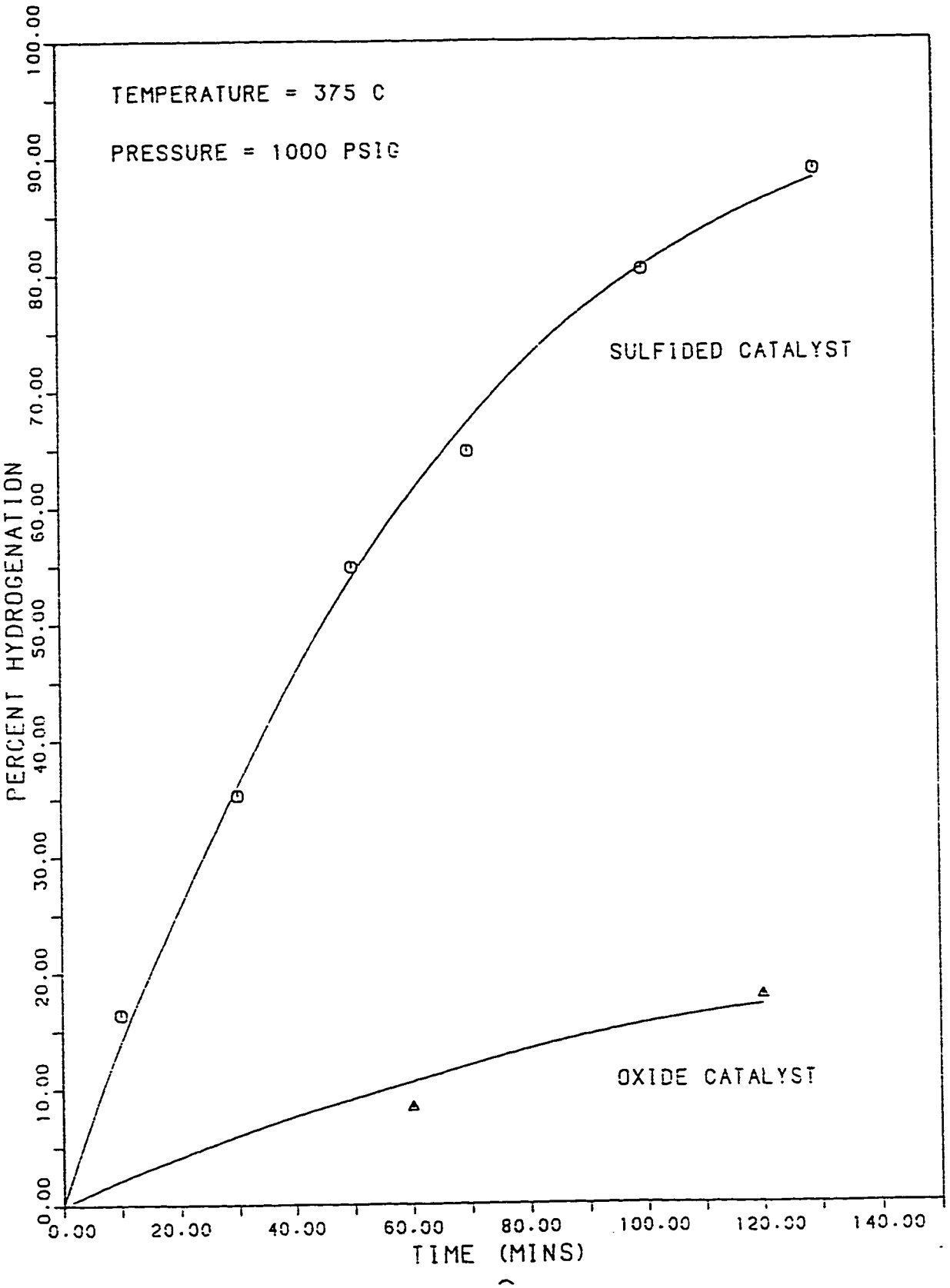


Figure 4.1.7 Comparison of Percent PBz Hydrogenation on Oxide and Sulfided $NiMo/Al_2O_3$ Catalysts at 375 °C

As described earlier, hydrogen sulfide, ammonia and water are formed under reaction conditions in real hydrotreators. In fact, they are final products of HDS, HDN and HDO. One of the objectives of this work is to study the effects of these compounds on catalytic hydrogenation of propylbenzene.

In order to achieve this objective, hydrogenation of propylbenzene was carried out in their presence. At each of the three temperatures (330, 350 and 375 °C), four runs were performed with the following feeds:

(1) Propylbenzene alone;
(2) Propylbenzene and hydrogen sulfide;
(3) Propylbenzene, hydrogen sulfide and ammonia; and
(4) Propylbenzene, hydrogen sulfide, ammonia and water.

Such a sequence was employed in order to elucidate the individual and combined effects of the presence of hydrogen sulfide, ammonia and water on the kinetics of catalytic hydrogenation of propylbenzene.

For the runs in which hydrogen sulfide and ammonia were present, they were generated, in situ, under reaction conditions. This was done by adding carbondisulfide and diaminoethane to the reaction mixture. These compounds are instantaneously and completely converted to hydrogen sulfide and ammonia under the reaction conditions (Section

3.). For the runs in which water was present, it was added to the reaction mixture. A partial pressure of 100 mmHg was maintained for each of these compounds for the runs in which their presence was needed.

A reproducibility run was carried out at 330 °C in the presence of hydrogen sulfide and ammonia over sulfided catalyst. Percent hydrogenation versus reaction time for the two runs is plotted in Figure 4.1.5. The results were reproducible within an accuracy of 3%. This run also proves the reproducible activity of presufided catalyst. It should be noted that a change in the sulfiding procedure can influence the hydrogenation activity of the catalyst.

Percent hydrogenation versus reaction time are plotted in Figures 4.3.1, 4.3.2 and 4.3.3 for the runs at 330, 350 and 375 °C, respectively. Each plot shows the curves for hydrogenation of propylbenzene alone, in the presence of hydrogen sulfide and in the presence of hydrogen sulfide and ammonia. These curves shows that the addition of hydrogen sulfide inhibits the hydrogenation. In the presence of hydrogen sulfide and ammonia the inhibition was much more pronounced. Addition of water to hydrogen sulfide and ammonia in the reaction mixture does not seems to influence the conversion, as the data points are almost overlapping with that of experiment with hydrogen sulfide

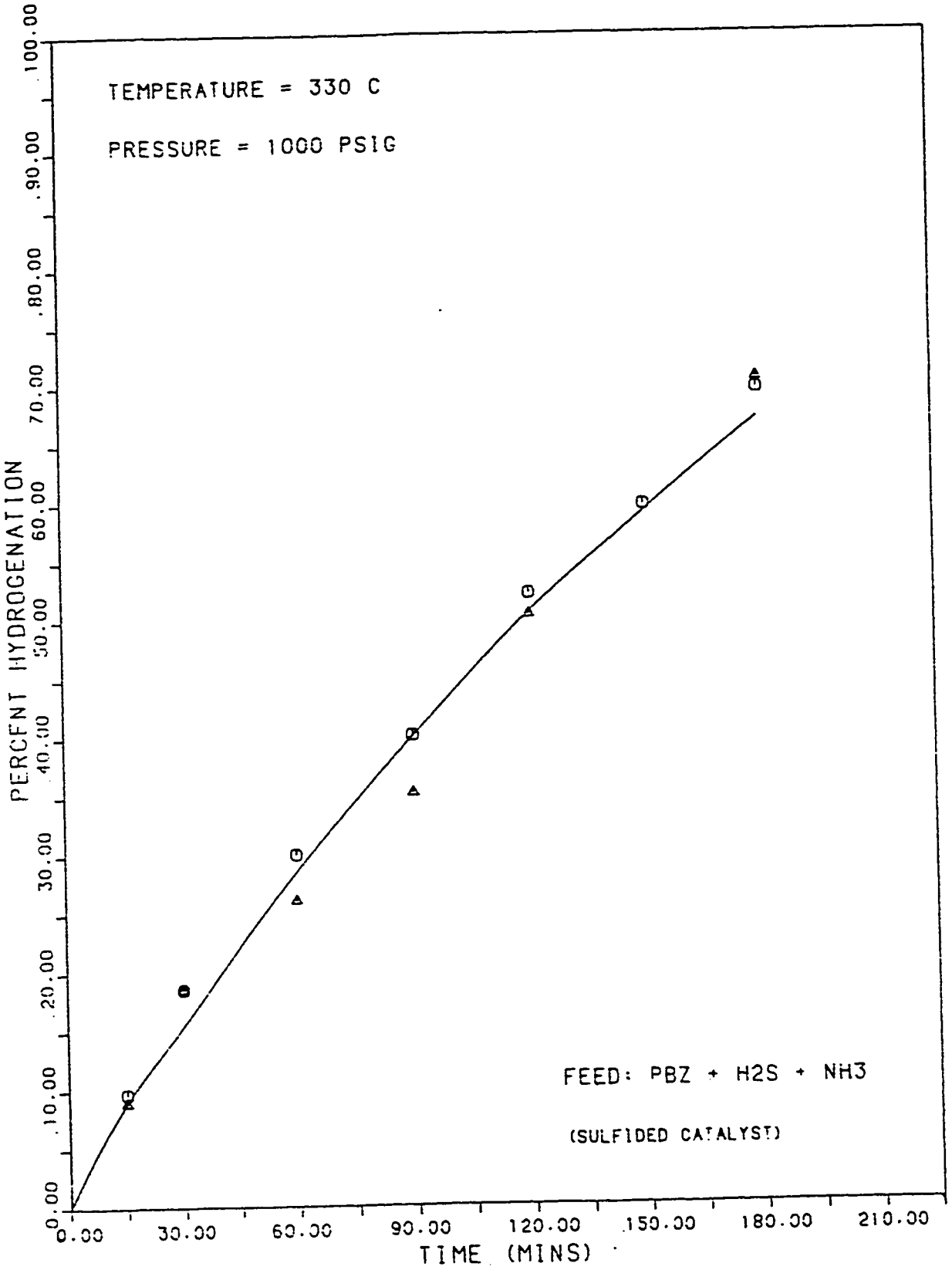


Figure 4.1. 8 Reproducibility of Data. PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst in the presence of H_2S and NH_3 at 330 °C

and ammonia. These trends were observed at all three temperatures studied.

Quantitative results and physical interpretations of these effects are given later (Section 4.2.2).

4.2 Discussions

This section is devoted to a discussion of results, with emphasis on translating the observed data into a rate equation that suitably represents the kinetics. Quantitative results and an interpretation of them, in the light of current understanding of the catalysis and chemistry of hydrogenation over hydroprocessing catalysts are given. A comparision with results of previous works is also presented.

4.2.1 Reaction Kinetics:

Heterogeneous catalytic reactions are usually much more complicated than chemical reactions in a homogeneous phase. The formation of surface complex is a prerequisite for surface catalysis, and kinetic equation must account for this. In addition to this, transport processes may influence the overall rate (Smith, 1981). In simple terms, the physical and chemical processes that must

proceed on a molecular scale are the following:

(1) Mass transfer of reactants from the bulk of the fluid to the surface of the catalyst particle;

(2) Diffusion of the reactants from the exterior surface to the interior surface of the catalyst particle, where the reaction occurs;

(3) Chemisorption of atleast one of the reactants on the catalyst surface;

(4) Reaction of species at the surface;

(5) Desorption of products and reactants from the surface;

(6) Diffusion of products from the pores of the external catalyst surface; and

(7) Mass transfer of products from the exterior of the catalyst to the bulk of the liquid.

Even if the rate controlling resistances of external and internal mass transfer and diffusion are eliminated, as was done in this study, the remaining adsorption, desorption and surface reaction steps are often sufficiently complex to prevent selection of straightforward reaction models which accurately desribe the reaction process. This is mainly due to the nonhomogeneity of the catalyst surface and active centers. Thus, the types of rate equations frequently encountered are highly simplified models which give acceptable fits to

the data (Carberry, 1976)

In developing rate expressions, one of the two assumptions is usually made:

(a) Adsorption equillibrium is maintained at all times, and the rate-determining step for the overall process is the rate of reaction on the surface; or

(b) The rate of surface reaction is rapid and adsorption or desorption is the rate determining step.

It is common to assume that the surface reaction is rate-controlling step and that the concentrations of adsorbed species are determined by adsorption equillibria as described by Langmuir isotherm. Reaction is assumed to occur between adsorbed species on the catalyst. If the reaction takes place between adsorbed A and adsorbed B, they must be adsorbed on the neighbouring sites for the reaction to occur. These assumptions lead to Langmuir-Hinshelwood type of kinetic expressions (Satterfield, 1980). The form and complexity of the expression depend on the assumptions made concerning the mechanism of adsorption and desorption.

For the catalytic hydrogenation of propylbenzene, in the presence of hydrogen sulfide, ammonia and water, the rate of reaction can be well formulated in terms of a Langmuir-Hinshelwood type of kinetic expession of the

following form:

$$r = \frac{k\, K_{PBz} P_{PBz}\, K_{H_2} P_{H_2}}{(1+K_{PBz}P_{PBz}+K_{H_2S}P_{H_2S}+K_{NH_3}P_{NH_3}+K_{H_2O}P_{H_2O})^2}$$

where K_i's are adsorption equillibrium constants and P_i's are partial pressures. The subcripts are

PBz = Propylbenzene, H_2 = Hydrogen,

H_2S = Hydrogen sulfide, NH_3 = Ammonia,

and H_2O = Water.

It is reported in literature that hydrogen is adsorbed on different type of sites than hydrocarbons (Sonnemans et al., 1973) and this hypothesis is taken into account in the above expression. Propylbenzene is not stongly adsorbed on the catalyst relative to other compounds. Hence, the second term in the denominator is negligible compared to the others. The expression then reduces to

$$r = \frac{k\, K_{PBz} P_{PBz}\, K_{H_2} P_{H_2}}{(K_{H_2S}P_{H_2S}+K_{NH_3}P_{NH_3}+K_{H_2O}P_{H_2O})^2}$$

The partial pressures of hydrogen sulfide, ammonia and water are held constant. Therefore, at constant temperature, the denominator is constant. The partial pressure of hydrogen is very large (1000 psig.) and it

remains almost constant throughout the reaction time. The rate expression is then reduced to a psuedo-first order expression:

$$r = k' P_{PBz}$$

where k' is the pseudo-first order reaction rate constant.

Based on similar arguments, the rate of many hydroprocessing reactions are reported to follow psuedo-first order kinetics in the literature: Shih et al. (1977) for reactions in quinoline HDN reaction network; Krishnamurthy et al. (1979) for reactions in dibenzofuran HDO reaction network; Sapre and Gates (1981) for hydrogenation of aromatic hydrocarbons; and Gultekin et al. (1984) for propylbenzene hydrogenation.

The results of the present work also follow a pseudo-first order kinetics at all conditions studied. First order plots are shown in Figures 4.2.1, 4.2.2, 4.2.3 and 4.2.4 for the conditions depicted thereon. Quantitative results and their interpretations are given in next section.

4.2.2 Quantitative results and their interpretations: The hydrogenation of propylbenzene on both oxide and sulfide forms of $NiMo/Al_2O_3$ catalyst was observed to follow

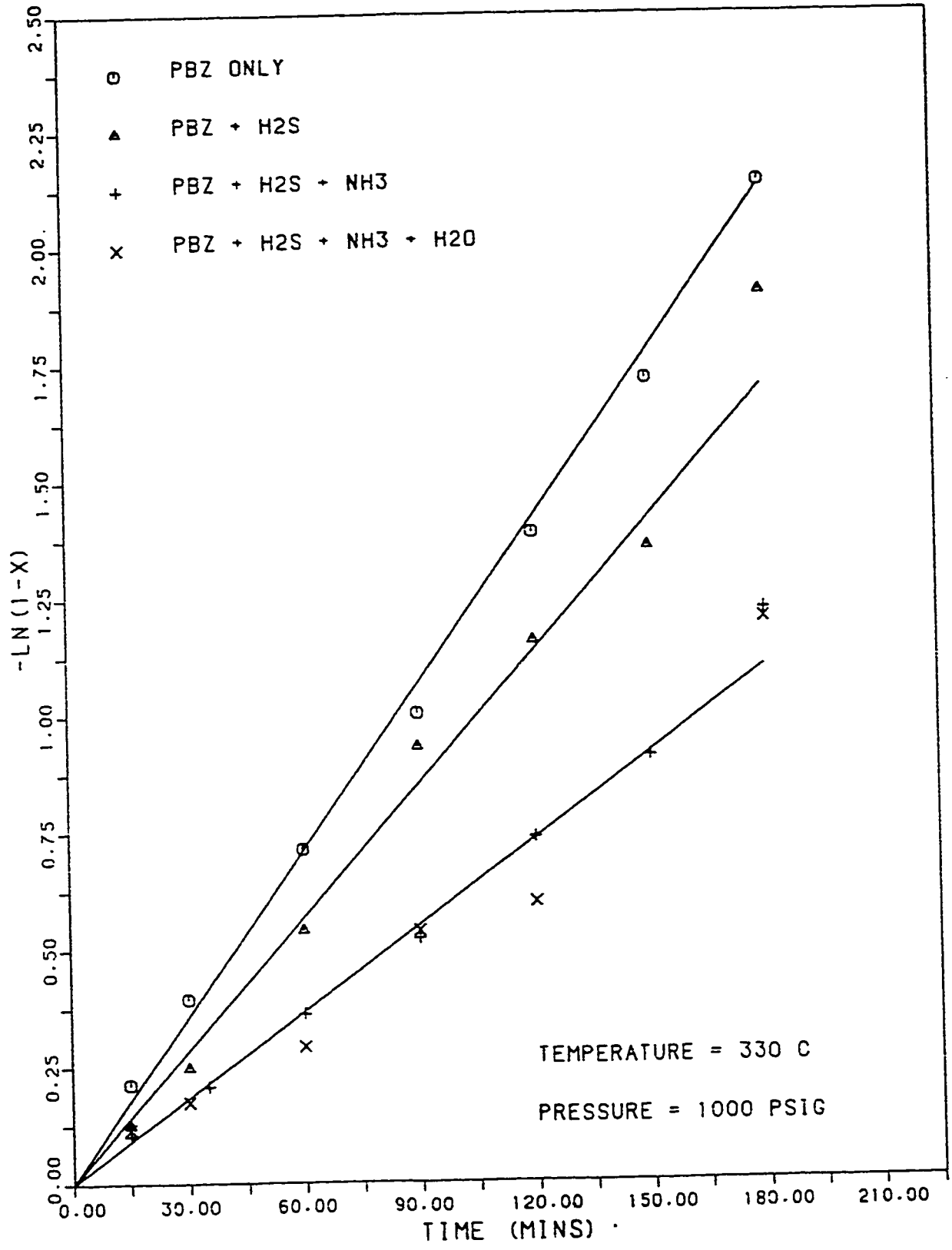


Figure 4.2.2 First order plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst at 330 °C

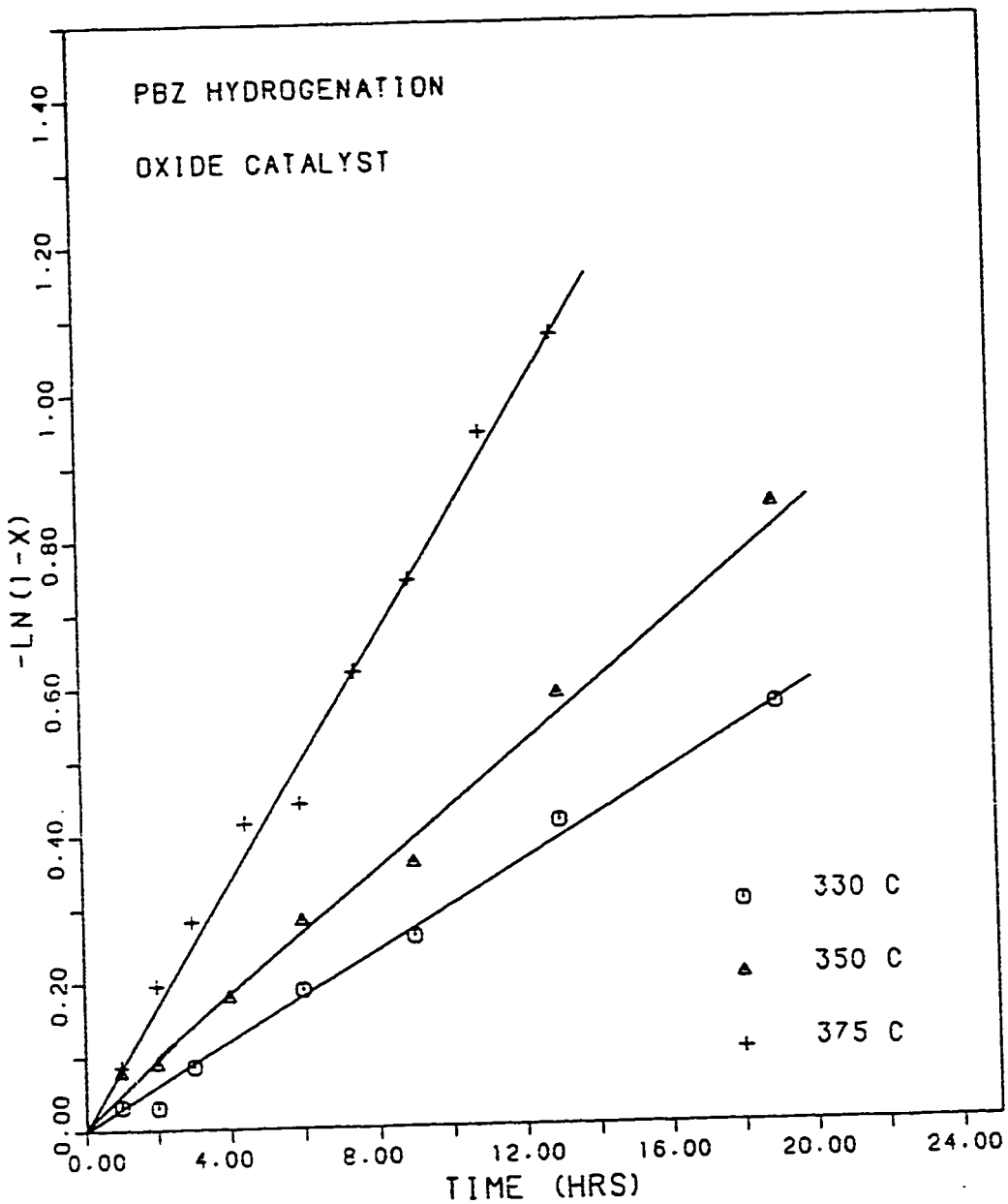


Figure 4.2.1 First order plot for PBz Hydrogenation on Oxide $NiMo/Al_2O_3$ Catalyst

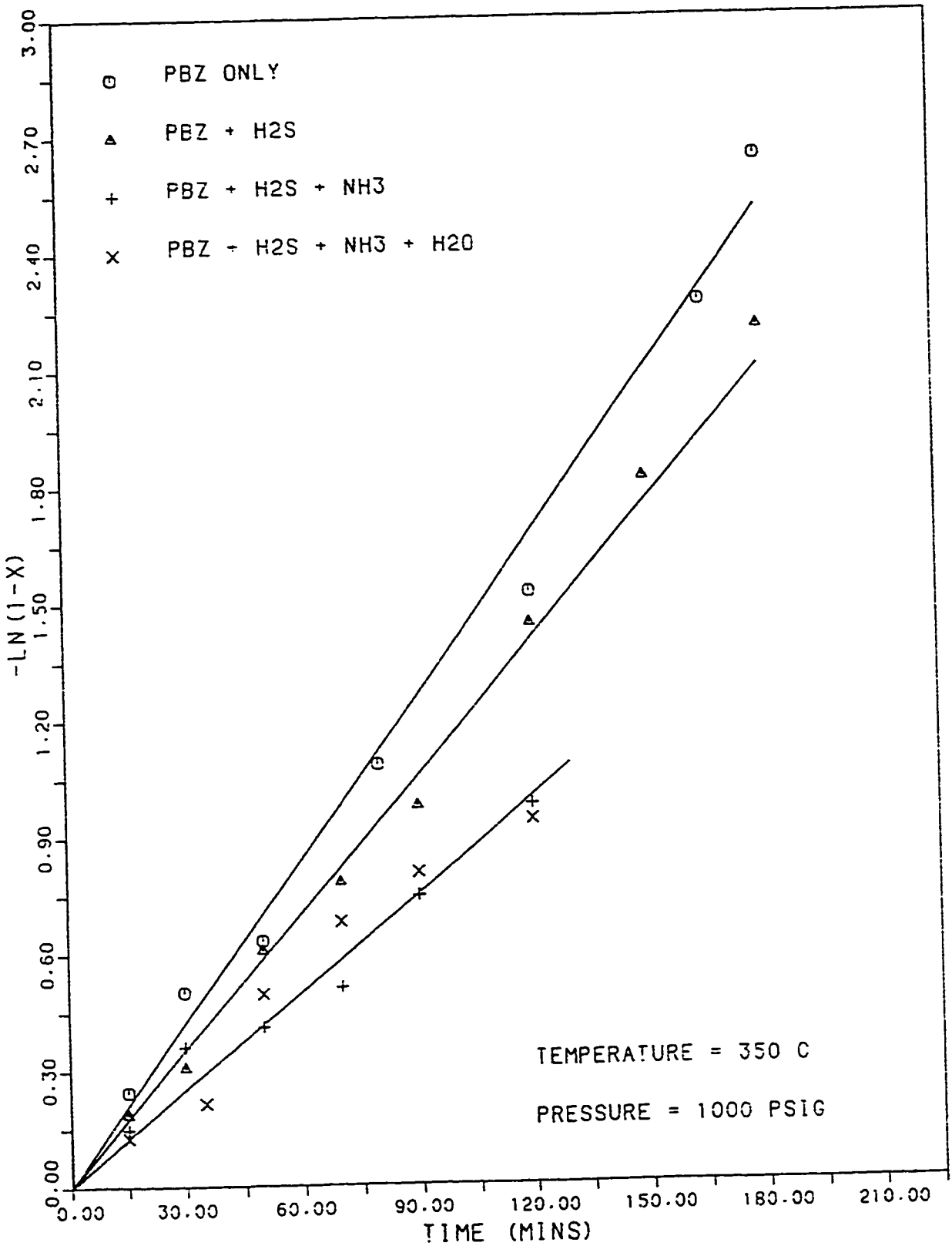


Figure 4.2.3 First order plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst at 350 °C

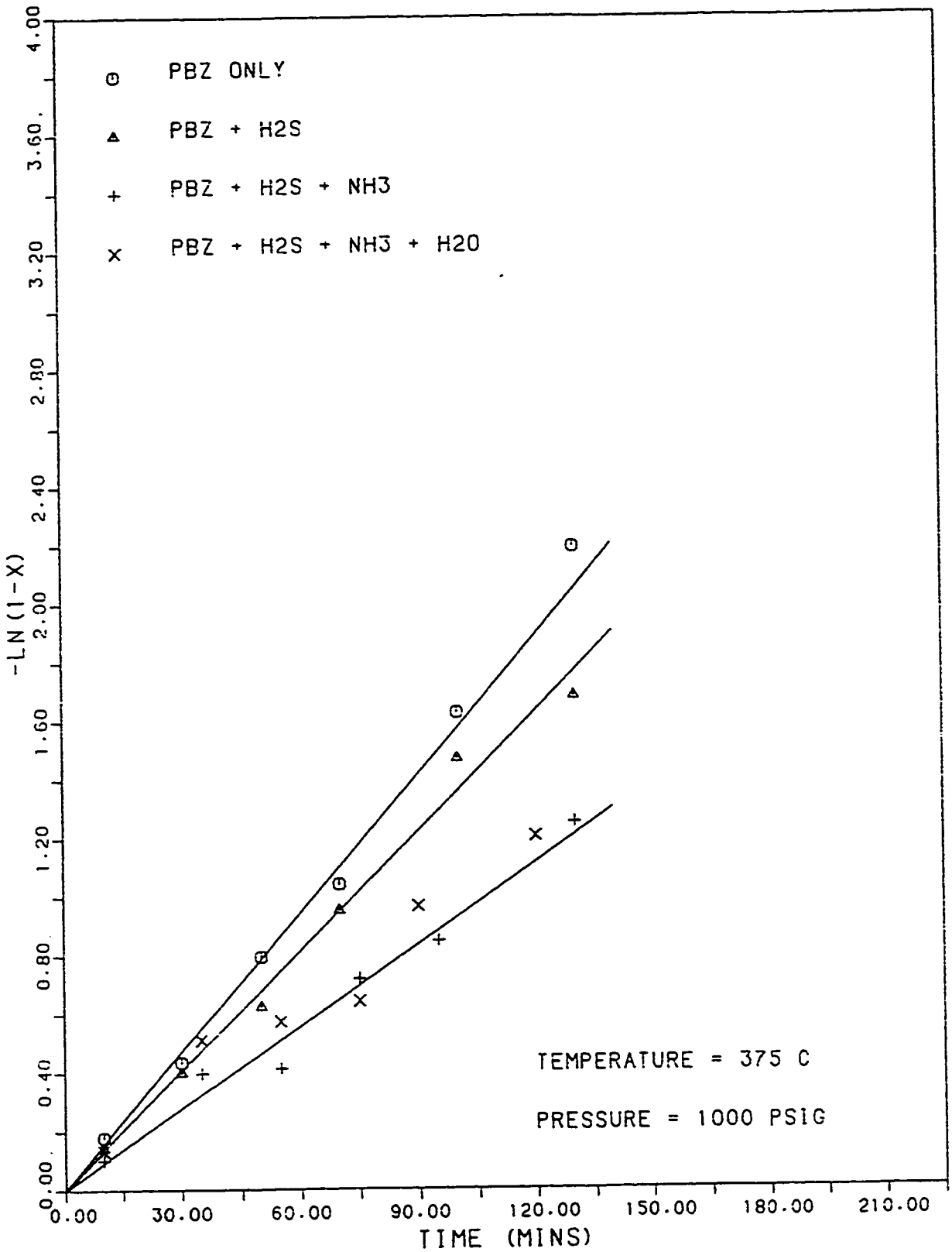


Figure 4.2.4 First order plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst at 375 °C

pseudo-first order kinetics in propylbenzene at all three temperatures studied. A similar result was obtained in the presence of hydrogen sulfide, hydrogen sulfide and ammonia, and hydrogen sulfide, ammonia, and water. These results are illustrated by first order plots in Figure 4.2.1 for experiments with oxide catalyst and in Figures 4.2.1, 4.2.2, 4.2.3 and 4.2.4 for experiments with sulfided catalyst at the conditions depicted theron.

The pseudo first order rate constants are estimated from the experimental data by linear least squares technique using a programmable calculator. The values of the reaction rate constants for all the runs, alongwith the feeds and reaction conditions, are summarized in Table 4.2.1.

Comparision of pseudo-first order reaction rate constants (Table 4.2.1) provides a quantitative information about the effect of the presence of hydrogen sulfide, ammonia and water and the effect of catalyst sulfiding on propylbenzene hydrogenation.

Effect of hydrogen sulfide: Results shows that due to the presence of hydrogen sulfide, the hydrogenation rate was reduced. The inhibition was in the range of 10-15 %, but there was no particular trend with variation in temperature. At 330 °C the inhibition was 12.8 %; at 350

Table 4.2.1

Pseudo-first Order Reaction Rate Constants

Feed	Temperature °C	Pseudo-first Order Rate Constant (m^3/kg.cat.sec x 10^6)
Oxide Catalyst		
PBz	330	0.534
PBz	350	0.703
PBz	375	1.433
Presulfided Catalyst		
PBz	330	12.307
PBz + H_2S	330	10.731
PBz + H_2S + NH_3	330	6.811
PBz + H_2S + NH_3 + H_2O	330	6.606
PBz	350	14.513
PBz + H_2S	350	12.996
PBz + H_2S + NH_3	350	8.306
PBz + H_2S + NH_3 + H_2O	350	8.569
PBz	375	34.630
PBz + H_2S	375	29.663
PBz + H_2S + NH_3	375	22.013
PBz + H_2S + NH_3 + H_2O	375	21.588

°C it reduces to 10.5 %, while at 375 °C it increases to 14.3 %. As noted earlier, the hydrogen sulfide partial pressure at all three temperatures was constant at 100 mmHg.

Inhibition of hydrogenation by hydrogen sulfide was observed by several investigators. It has been postulated that sulfur-anion vacancies, exposing Mo cations, acts as active sites for hydrogenation. Due to the presence of hydrogen sulfide in the reaction medium some of these vacancies are "filled in", thus reducing the number of sites.

Effect of hydrogen sulfide and ammonia: In the presence of hydrogen sulfide and ammonia, the rate of propylbenzene hydrogenation was greatly reduced. The inhibition was in the range of 35-45 %. There was a decrease in inhibition with temperature. At 330 °C the inhibition was 44.7%; at 350 °C it decreases to 42.8% while at 375 °C it further declined to 36.4%.

Ammonia, being highly basic, is competatively adsorbed on the acidic sites. This reduces the number of active centers available for adsorption of propylbenzene. Since this inhibition is due to simultaneous presence of hydrogen sulfide and ammonia, this effect is in addition to that of filling up of sulfur vacancies by hydrogen

sulfide. The decrease in the rate of inhibition with temperature can also be explained by the competative adsorption phenomena.

Addition of water to hydrogen sulfide and ammonia does not seems to influence the rate of hydrogenation. Although there is a slight variation (about 3%), but it can be an artifact of experimental inaccuracy.

This result suggests that, in the presence of hydrogen sulfide and ammonia, water is not adsorbed on the catalyst surface.

Effect of sulfiding; It is known that sulfided form of catalyst is more active than oxide catalyst. Results of the present work shows that the hydrogenation activity of $NiMo/Al_2O_3$ catalyst enhances by 20-25 times due to sulfiding.

This enhancement may be due to the increase in active centers, which are Mo^{+3} cations. However, the structure of the sulfided catalyst may be entirely different from that of the oxide catalyst from which it is formed, as reported by Schuit and Gates (1973).

Another observation was that with sulfided catalyst cracking of hexadecane was almost zero, in contrast to that with oxide form of catalyst. Different effects of

sulfiding shows that the active centers responsible for hydrogenation and hydrogenolysis are different.

Apparent activation energy: Having the pseudo-first order reaction rate constants at three temperatures, apparent activation energies were determined. This has been done by drawing the Arrhenius plots, as shown in Figures 4.2.5 to 4.2.9 for various conditions depicted thereon. The apparent activation energies are summarized in Table 4.2.2. All apparent activation energies are found to be in the range of 17-21 kcal/gmol.

Comparision of values of apparent activation energies provide some interesting conclusions.

* The apparent activation energies are almost same in the absence and presence of hydrogen sulfide for experiments over sulfided catalyst. This explains the claim that the inhibition due to hydrogen sulfide is not due to competative adsorption.

* The apparent activation energies for the runs in which ammonia is present is about 2.5 kcal/gmol more than for the runs in which ammonia was not present. This confirms that ammonia is competing for the same active sites as propylbenzene.

* Addition of water to hydrogen sulfide and ammonia does not change the apparent activation energy. Hence, it can be surmised that, in the presence of hydrogen sulfide and

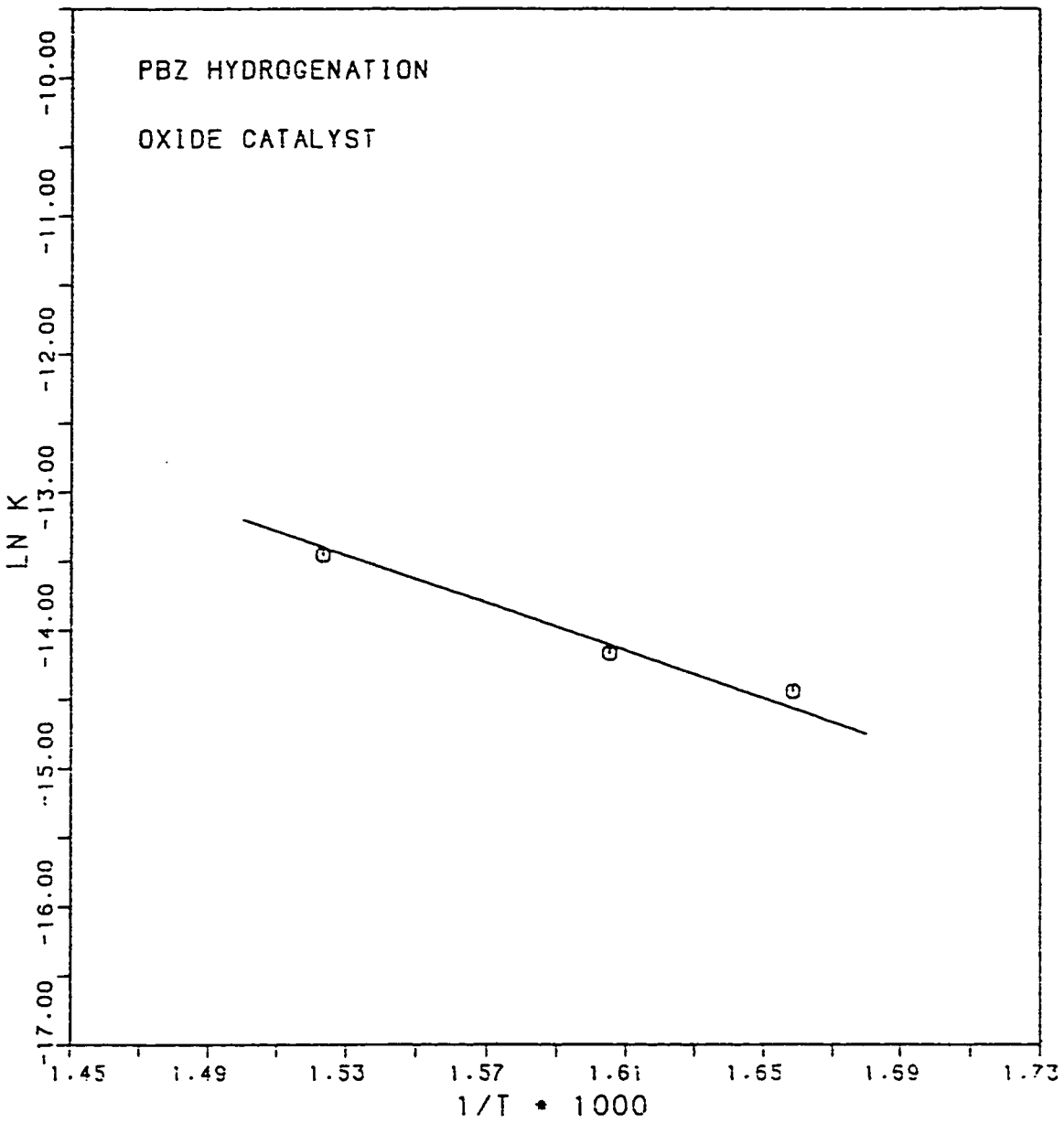


Figure 4.2.5 Arrhenius Plot for PBz Hydrogenation on Oxide $NiMo/Al_2O_3$ Catalyst

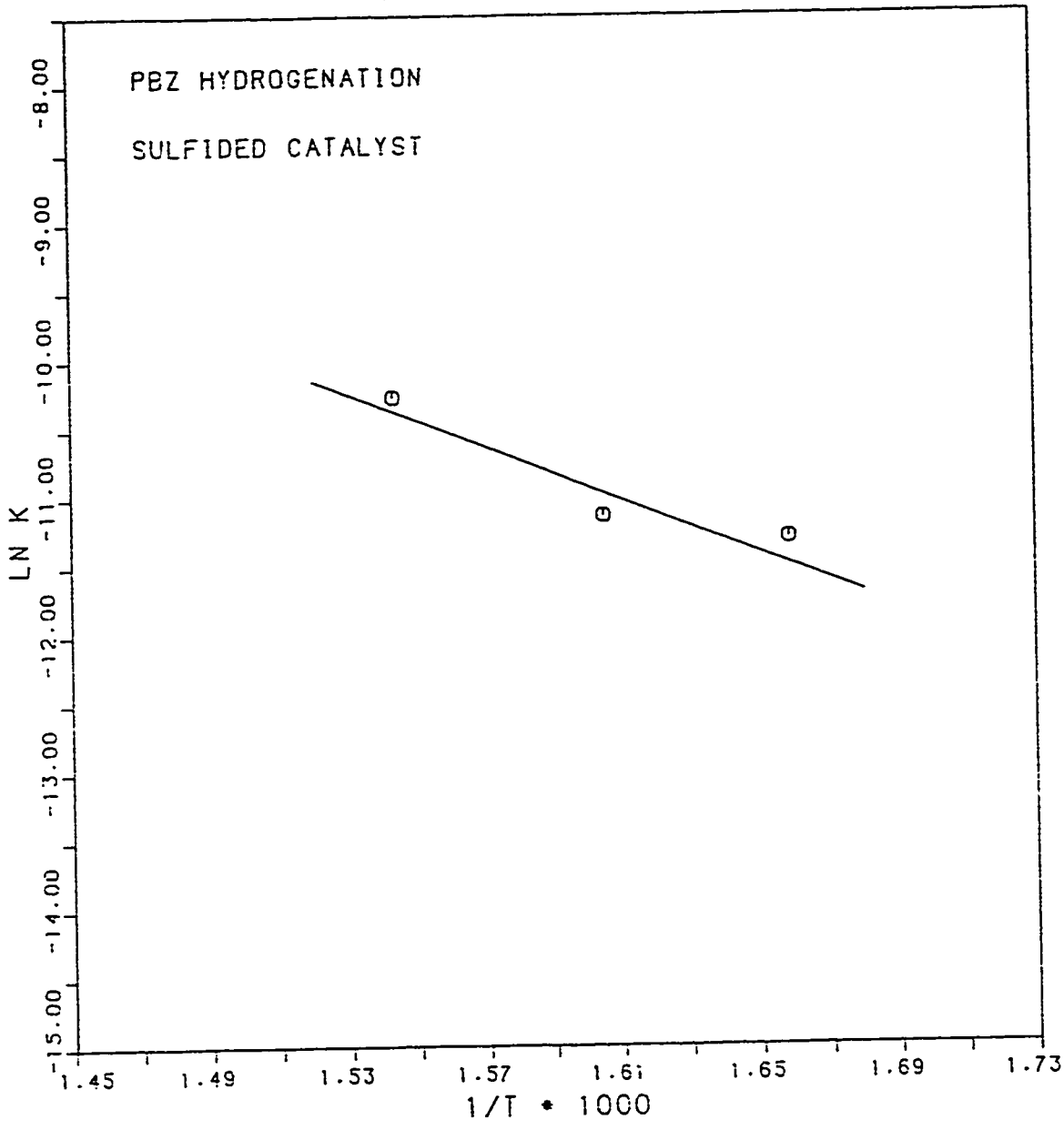


Figure 4.2.6 Arrhenius Plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst

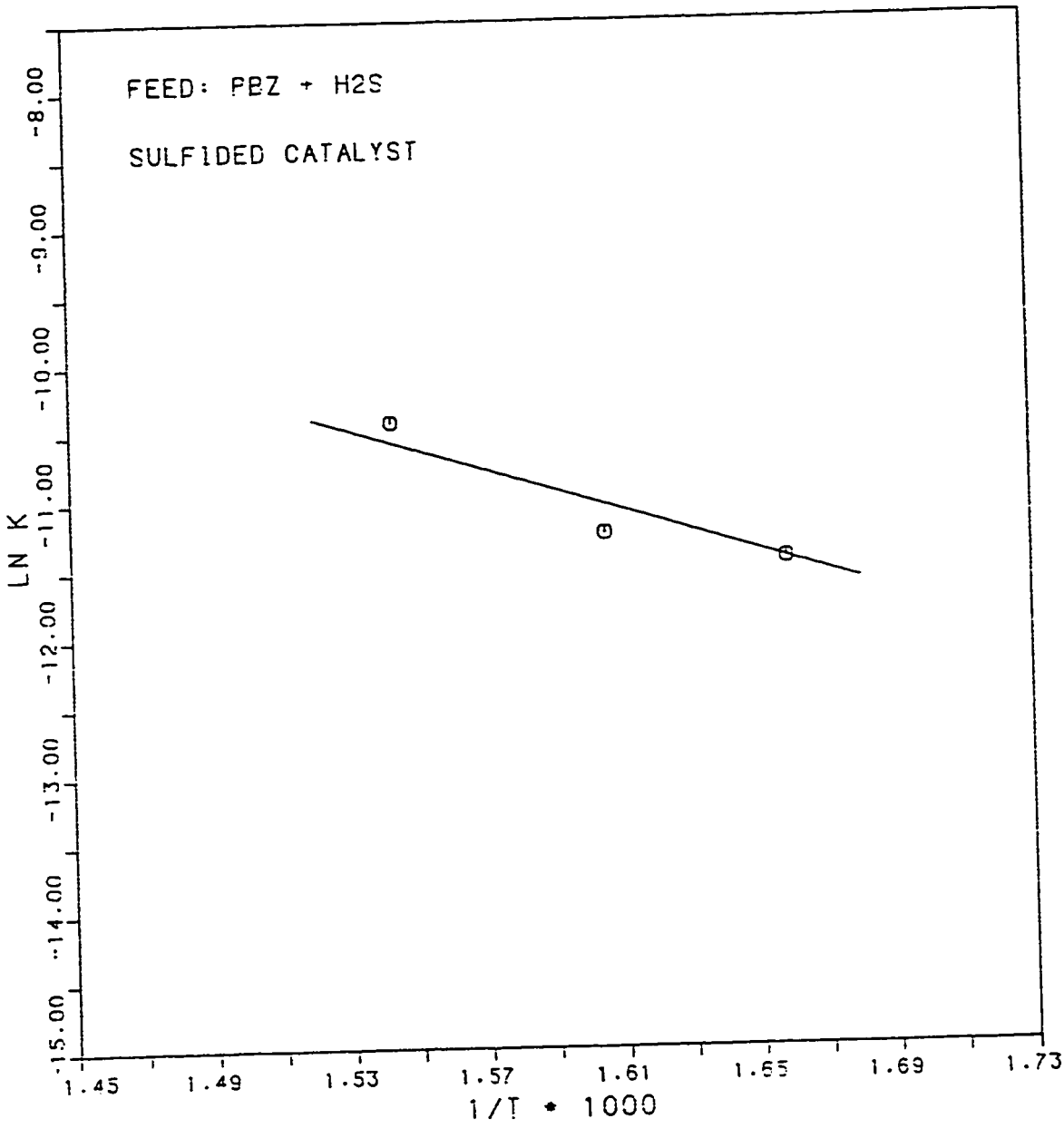


Figure 4.2.7 Arrhenius Plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst in the Presence of Hydrogen Sulfide

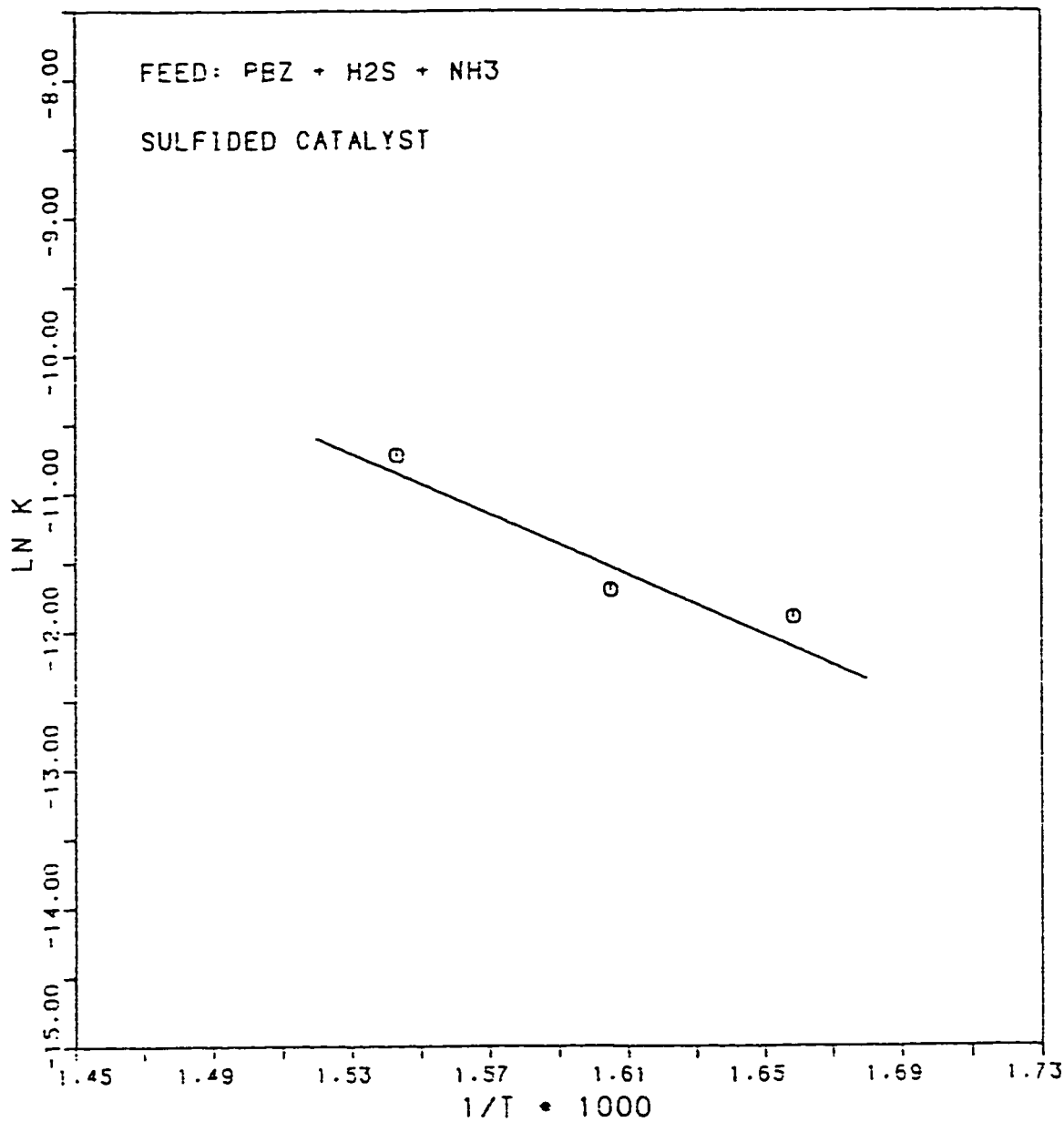


Figure 4.2.8 Arrhenius Plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst in the presence of Hydrogen Sulfide and Ammonia

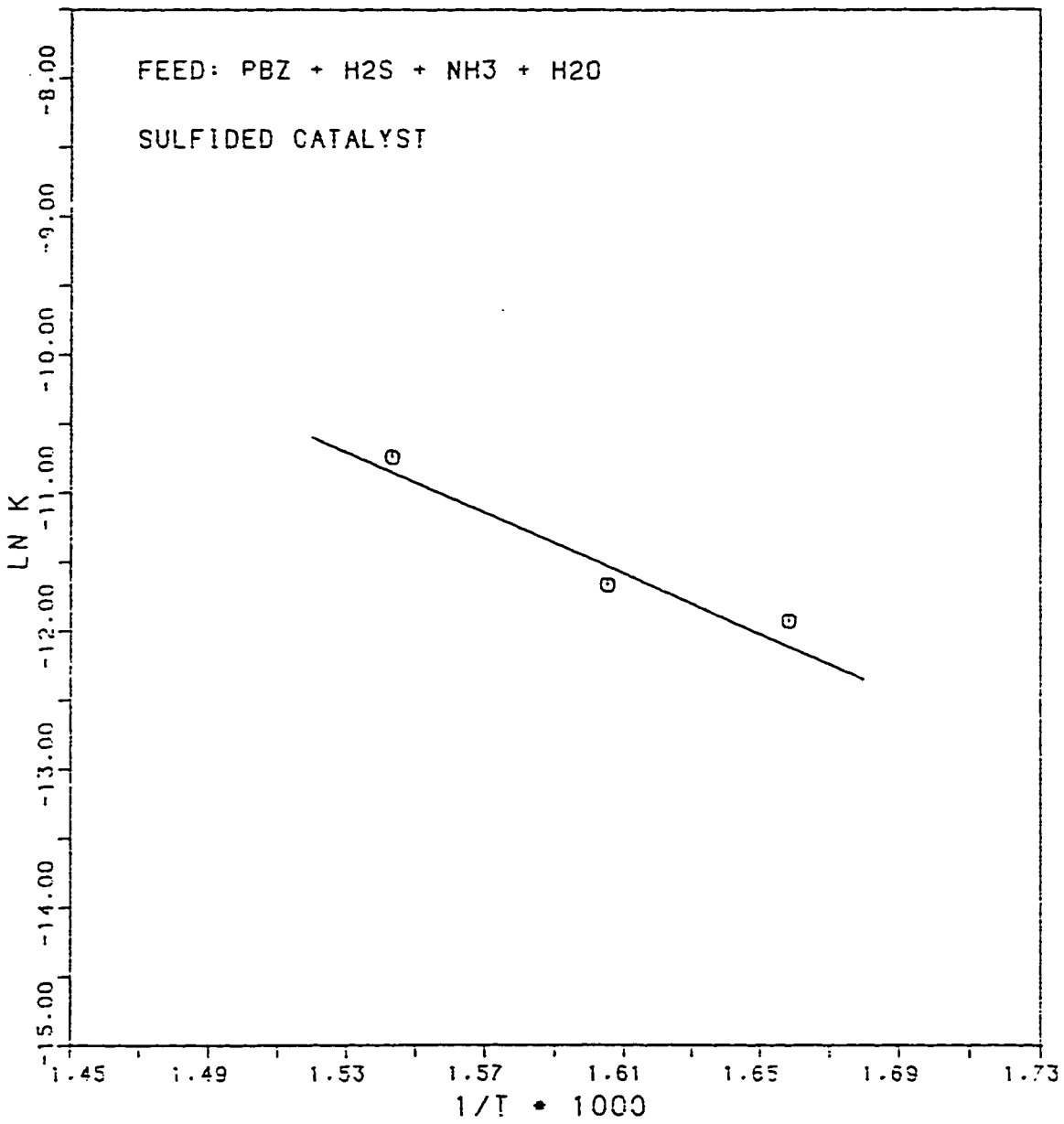


Figure 4.2.9 Arrhenius Plot for PBz Hydrogenation on Sulfided $NiMo/Al_2O_3$ Catalyst in the Presence of Hydrogen Sulfide, Ammonia

Table 4.2.2

Apparent Activation Energies

Feed	Catalyst Form	Apparent Activation Energy (kcal/gmol)
PBz only	Oxide	17.18
PBz only	Presulfided	18.11
PBz + H_2S	Presulfided	17.94
PBz + H_2S + NH_3	Presulfided	20.53
PBz + H_2S + NH_3 + H_2O	Presulfided	20.69

ammonia, water is not adsorbed on the catalyst surface.

4.2.3 Comparision with literature:

In this section, results of this work are compared with information available from related literature.

In a very recent publication, Gultekin et al. (1984) reported the results of their studies of the effects of hydrogen sulfide and ammonia on catalytic hydrogenation of propylbenzene. At all reaction conditions and for all feed mixtures studied, pseudofirst order kinetics is observed to follow. Inhibition by hydrogen sulfide is reported, but the inhibition was much more pronounced than that observed in the present work. This may be due to the reason that experiments were carried out in a continous flow microreactor. Moreover the catalyst:reactant ratio is higher in this study, which results in higher number of active centers even after the competative adsorption by ammonia. Addition of ammonia resulted in much more pronounced inhibition than that observed in the present work. This can also be explained by the same reasoning as suggested for hydrogen sulfide inhibition.

Kinetics of hydrogenation of several aromatic hydrocarbons catalyzed by $CoMo/Al_2O_3$ were reported by Sapre and Gates (1981). The kinetics were presented as

psuedo-first order in hydrocarbon reactant, as was done in this study. The magnitude of pseudo-first order rate constant obtained for propylbenzene hydrogenation on sulfided $NiMo/Al_2O_3$ is compared with the reported value by Sapre and Gates (1981). For benzene hydrogenation over sulfided $CoMo/Al_2O_3$ catalyst at 325 °C and 70 atm., they reported a value of 3×10^{-6} m^3/kg.cat. sec. The value obtained under similar conditions (330 °C vs. 325 °C and 68 atm vs. 70 atm.) is 12×10^{-6}) m^3/kg.cat.sec. Although the order is same, but a four fold increase in the rate can be attributed to the fact that $NiMo/Al_2O_3$ is more active for hydrogenation than $CoMo/Al_2O_3$ (Gates et al., 1978).

Apparent activation energies obtained in this study are in the range of 17-22 kcal/gmol for different feeds. These are consistent with some other previously reported values. For cyclohexene hydrogenation over bulk and supported WS_2 catalysts, Voorhoeve and Stuiver (1971) found the apparent activation energies in the range of 15-22 kcal/gmol. Shih et al. (1977) reported the values of apparent activation energies in the range of 16-18 kcal/gmol for different hydrogenation reactions involved in the reaction network of quinloine HDN over $NiMo/Al_2O_3$.

There are few studies involving hydrogenation of the benzenoid ring of nitrogen- and sulfur- containing

compounds. A brief discussion of these studies, in the light of results of present work, follows.

In a detailed study, Gultekin (1980) observed the effects of hydrogen sulfide on various reactions involved in quinoline HDN reaction network. It was found that addition of hydrogen sulfide substantially enhanced the hydrogenolysis reactions but moderately inhibited hydrogenation reactions. An increase of partial pressure of hydrogen sulfide above 13.3 kPa caused no further effects. The inhibiting effect of hydrogen sulfide on hydrogenation of propylbenzene is thus consistent with this study.

Goudriaan (1974) reported that complete ring hydrogenation of pyridine is first order in pyridine over sulfide $CoMo/Al_2O_3$. Hydrogen sulfide partial pressures upto 1 atm. resulted in a 35% decrease in the first order rate constant at 250 °C and a 17% decrease at 300 °C. However, from 1 atm to 11 atm hydrogen sulfide partial pressure, the hydrogenation rate remains essentially constant. This result is indicative of hydrogen sulfide inhibition at low concentration. Goudriaan concluded that simple competitive adsorption between hydrogen sulfide and pyridine could not explain the overall effect of hydrogen sulfide on pyridine hydrogenation.

Rates of hydrogenation reactions in the quinoline reaction network were represented by pseudo-first order rate constants by Shih et al. (1977). Three catalysts were used, one of which was $NiMo/Al_2O_3$. When the catalyst was sulfided, addition of 0.05 wt% carbon disulfide to the reaction mixture gave no change in the rate of hydrogenation for the $CoMo/Al_2O_3$ catalyst. But $NiMo/Al_2O_3$ catalyst showed some hydrogen sulfide inhibition of the hydrogenation reactions.

From the hydrodesulfurization literature (Gates et al., 1979), it is believed that active sites on sulfided $CoMo/Al_2O_3$ responsible for hydrodesulfurization are sulfur anion vacancies exposing Mo^{+3} cations. The inhibition of hydrogen sulfide on such sites is represented by the following reaction (Gates et al., 1979):

$$2Mo^{3+} + H_2S + \#_s \longrightarrow H_2 + 2Mo^{4+} + S^{2-}$$

where $\#_s$ represents a sulfur-ion vacancy.

As hydrogen sulfide also inhibits hydrogenation, it appears that Mo^{3+} ion are the active sites responsible for hydrogenation. Voorhoeve and Stuiver (1971) also suggested that the active sites for benzene hydrogenation were W^{3+} ions coordinated by four sulfur ions. Thus, it appears that sulfur anion vacancies are responsible for both hydrogenation and hydrodesulfurization.

Much of the evidence supporting the proposition of different catalytic sites is the result of poisoning and adsorption studies with hydrogen sulfide and nitrogen-containing compounds of varying basicities. In Chapter Two several studies were described indicating the evidence of different kinds of sites for hydrogenation and hydrogenolysis.

Desikan and Amberg (1961) proposed two sites of differing acidity: the first was a strongly acidic site charecterized by activity for hydrogenation of olefins and competitive adsorption of hydrogen sulfide and pyridine; the second was a weaker acid site most active in desulfurization and poisoned by strong base such as ammonia.

Lee and Butt (1977), from a study of the poisoning of thiophene hydrodesulfurization and butene hydrogenation by pyridine, noted a similarity in poisoning at low concentrations of pyridine but a divergence at higher concentrations. They concluded that the sites for hydrogenation and hydrogenolysis were similar but not the same.

The results of this study also indicate that strongly basic ammonia poison the hydrogenation reaction catalyzed by $NiMo/Al_2O_3$. Thus, there is a general agreement that

hydrogenation sites are more stongly acidic than hydrogenolysis sites as shown repeatedly by the stronger interaction of former with basic nitrogen compounds.

In brief, the current understanding of catalytic chemistry on sulfide catalysts indicates that hydrogenation and hydrogenolysis occur on different types of anion vacancies and the nature of the differences are not fully understood at the present time. The questions of strength (as well as number) of vacancies, their further charecterization in terms of adsorbed complexes, and specific roles of poisons and coke await further investigations.

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Chapter V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

(1) Preliminary experiments showed that at a hydrogen pressure of 500 psig. with oxide form of catalyst, the hydrogenation of propylbenzene proceeds at an undetectable rate. At 1000 psig. the rate was appreciable and hence the rest of the experiments were carried out at a pressure of 1000 psig.

(2) The analysis of products showed propylcyclohexane as the only product of propylbenzene hydrogenation. No other product, such as propylcyclohexene, was observed. Possible dealkylated products, such as benzene or cyclohexane etc., were also not found. This allows the calculation of conversion based on disappearence of propylbenzene. When the experiments were carried out with oxide form of catalyst, some hexadecane cracked giving a number of short-chain paraffins.

(3) The hydrogenation of propylbenzene on both oxide and presulfided forms of $NiMo/Al_2O_3$ catalyst was observed to follow pseudo-first order kinetics in propylbenzene at all three temperatures studied. A similar result was obtained in the presence of hydrogen sulfide, hydrogen

sulfide and ammonia, and hydrogen sulfide, ammonia, and water.

(4) Results shows that due to the presence of hydrogen sulfide, the hydrogenation rate was reduced by 10-15 %. It has been postulated that sulfur-anion vacancies exposing Mo^{3+} cations, acts as active centers for hydrogenation, which are partilly 'filled in' in the presence of hydrogen sulfide.

(5) In the presence of hydrogen sulfide and ammonia, the rate of propylbenzene hydrogenation was greatly inhibited. The inhibition was 44.7% at 330°C, 42.8% at 350 °C and 36.4% at 375 °C. Highly basic ammonia is competitivily adsorbed on the acidic sites. This reduces the number of active sites available for adsorption of propylbenzene. The decrease in inhibition with temperature can also be explained by competitive adsorption phenomena.

(6) Addition of water to hydrogen sufide and ammonia does not influence the rate of hydrogenation. This result suggests that, in the presence of hydrogen sulfide and ammonia, water is not competitivily adsorbed on the catalyst surface.

(7) Comparision of oxide and presulfided $NiMo/Al_2O_3$ shows that the hydrogenation activity enhances by 20-25 times due to sulfiding. Another observation was that with

presulfided form cracking of hexadecane was almost zero while that with oxide form some of the hexadecane cracked. Different effects of sulfiding suggests that the active centers responsible for hydrogenation and hydrogenolysis are not the same.

(8) All apparent activation energies are found to be in the range of 17-21 kcal/gmol. These values are consistent with reported values in literature for hydrogenation of aromatics on supported catalysts. Comparision of values of apparent activation energies provide some interesting conclusions:

i) The apparent activation energies are almost same in the absence and presence of hydrogen sulfide for experiments over presulfided catalyst. This explains the claim that the inhibition due to hydrogen sulfide is not due to competative adsorption.

ii) The apparent activation energies for the runs in which ammonia is present is about 2.5 kcal/gmol more than for the runs in which ammonia was not present. This confirms that ammonia is competing for the same active sites as propylbenzene.

iii) Addition of water to hydrogen sulfide and ammonia does not change the apparent activation energy. Hence, it can be surmised that, in the presence of hydrogen sulfide and ammonia, water is not adsorbed on the catalyst surface.

5.2 Recommendations

(1) Interaction studies were carried out under a limited range of concentrations and operating conditions in this research. Variation of the concentrations of aromatic hydrocarbon, H_2S, NH_3 and H_2O and of catalyst/reactant ratio will provide better understanding of the effects of these compounds on the chemistry and catalysis of the aromatic hydrogenation.

(2) The hydrogen pressure was limited by the cylinder pressure (maximum 2000 psig.). As heavier feedstocks require higher hydrogen pressures, it is recommended to study at higher pressures. The reactor system is capable of withstanding pressures upto 6000 psig. and such high pressures can be achieved by using a pump.

(3) A batch autoclave reactor was used in this study for its simplicity and the short experimental time associated with its use. A liquid-phase flow microreactor can be used for further studies. Such a reactor will enable a steady-state operation, in-situ sulfiding and catalyst deactivation studies.

(4) A modification in the existing Gas Chromatograph is desired to make it capable of using capillary columns. This will be very helpful in the resolution of complex mixtures. An autosampler will be useful when flow

reactors will be used.

(5) All the work in thesis was done with $NiMo/Al_2O_3$ commercial hydrotreating catalyst. Further experiments to determine the applicablity of the kinetic results of this work to other commercial catalysts such as $CoMo/Al_2O_3$ and NiW/Al_2O_3 are suggested.

(6) Acidity of hydroprocessing catalyst is a poorly understood subject. The present study does not through any light on the hydrogenolysis activity, except that its presnce was observed. A study of hydrogenolysis and its interactions with nitrogen-containing compounds of varying basicities will be helpful in understanding the nature of acidic sites.

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APPENDICES

[A] Determination of Response Factor

The response of Thermal Conductivity Detector (TCD) is given as area counts (arbitrary units) in the analysis report by the VISTA 402 Chromatography Data System. The number of area counts is a function of the amount of the compound injected as a sample. In order to determine the relation between the amount of propylbenzene injected and the area counts of propylbenzene peak, a standard sample was prepared. The standard sample contains 1 wt% of propylbenzene dissolved in n-hexadecane.

At the standard operating conditions of Gas Chromatograph (Table 3.3.1), different volumes of this standard sample is injected and its its response as the number of area counts noted. The volumes and the corresponding area counts are given in the following table:

Volume injected (mic. lit)	Equivalent gmol of PBz x 10^{-8}	Area Counts (arbitrary units) x 10^{5}
0.3	1.934	1.733
0.5	3.223	2.868
0.8	5.157	4.259
1.0	6.446	5.274
1.0	6.446	5.345

Linear relationship between area counts and moles of propylbenzene injected was observed. The response factor

is 1.167×10^{-13}. This implies that each area count of propylbenzene represents 1.167×10^{-13} gram moles of propylbenzene in the sample.

[B] Sample Calculation

Liquid samples were taken out periodically from the reactor during the runs and were analyzed by Gas Chromatography. A sample size of one microliter was injected at all times. The number of gram moles of propylbenzene in a sample was calculated by the area counts of propylbenzene peak using the response factor (Appendix A). The concentrations of propylbenzene in gm.moles/lit. is then calculated. The concentration of propylbenzene versus reaction time is plotted and the initial concentration is evaluated by extrapolation.

Based on the disappearance of propylbenzene, the conversion at any time t was calculated using the following equation:

$$X_{PBz} = \frac{C_{PBz_o} - C_{PBZ_t}}{C_{PBz_o}}$$

From the conversion data the values of $-\ln(1 - X_{PBz})$ were calculated. Linear least squares technique using a programmable calculator was employed for the evaluation of pseudo-first order reaction rate constants.

Having the psuedo-first order constants, Arrhenius plots and drawn and apparent activation energy is calculated from its slope.

As an example, for the Run # 4 one microliter of the sample after 60 mins. of reaction time gives 2.317×10^{5} area counts. From the response factor, this corresponds to 2.704×10^{-8} gmoles of propylbenzene. Hence the concentration is 2.704×10^{-2} gram moles/liter. Similarily, the concentrations at different reaction times are calculated. These values are plotted as a function of time and expolated to evaluate the initial concentration. The initial concentration of propylbenzene is found to be 5.500×10^{-2} gm.moles/lit. Using this value the conversion is calculated as 0.508 and $-\ln(1- X_{PBz})$ as 0.709. Having these values for all the samples, pseudo-first order reaction rate constant is calculated and its value was 1.969×10^{-4} sec^{-1}. For the catalytic reactions, the rate constant is usually based on the weight of catalyst per unit volume of reactant. Hence the rate constant for Run # 4 is 12.307×10^{-6} m^3/kgcat.sec.

A summary of experimental data is given in Appendix C.

C. Summary of Data

The following pages present a summary of experimental data. The runs were carried out at the following conditions:

Run #	Feed	Temp. °C	Pressure, psig
Oxide Catalyst			
1	PBz	330	1000
2	PBz	350	1000
3	PBz	375	1000
Presulfided Catalyst			
4	PBz	330	1000
5	PBz + H_2S	330	1000
6	PBz + H_2S + NH_3	330	1000
6B	PBz + H_2S + NH_3	330	1000
7	PBz + H_2S + NH_3 + H_2O	330	1000
8	PBz	350	1000
9	PBz + H_2S	350	1000
10	PBz + H_2S + NH_3	350	1000
11	PBz + H_2S + NH_3 + H_2O	350	1000
12	PBz	375	1000
13	PBz + H_2S	375	1000
14	PBz + H_2S + NH_3	375	1000
15	PBz + H_2S + NH_3 + H_2O	375	1000

Run # 1

Feed: PBz only

Conditions: 330 °C, 1000 psig

Catalyst: Oxide $NiMo/Al_2O_3$

Time (hrs)	Area Counts of PBz $\times 10^{-5}$	Conc. of PBz gmol/lit $\times 10^{2}$	Conversion X_{PBz}
0	--	4.850	0.000
1	4.023	4.699	0.032
2	4.035	4.708	0.029
3	3.819	4.457	0.081
6	3.444	4.019	0.171
9	3.211	3.747	0.227
13	2.752	3.212	0.338
19	2.352	2.749	0.433

$$k = 0.085 \times 10^{-4} \text{ sec}^{-1}$$

$$= 0.534 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 2

Feed: PBz only

Conditions: 350 °C, 1000 psig

Catalyst: Oxide $NiMo/Al_2O_3$

Time (hrs)	Area Counts of PBz $\times 10^{-5}$	Conc. of PBz gmol/lit $\times 10^{2}$	Conversion X_{PBz}
0	--	5.700	0.000
1	4.516	5.270	0.075
2	4.463	5.208	0.086
4	4.083	4.765	0.164
6	3.683	4.298	0.246
9	3.413	3.983	0.301
14	2.721	3.877	0.443
19	2.109	3.176	0.568

$$k = 0.112 \times 10^{-4} \text{ sec}^{-1}$$

$$= 0.703 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 3

Feed: PBz only

Conditions: 375 °C, 1000 psig

Catalyst: Oxide $NiMo/Al_2O_3$

Time (hrs)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0.0	--	5.300	0.000
1.0	4.165	4.861	0.083
2.0	3.732	4.355	0.178
3.0	3.421	3.992	0.247
4.5	2.999	3.499	0.339
6.0	2.923	3.411	0.356
7.5	2.445	2.853	0.462
9.0	2.162	2.523	0.524
11.0	1.773	2.069	0.610
13.0	1.553	1.813	0.658

$$k = 0.229 \times 10^{-4} \text{ sec}^{-1}$$

$$= 1.433 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 4

Feed: PBz only

Conditions: 330 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	5.500	0.000
15	3.815	4.452	0.191
30	3.030	3.536	0.357
60	2.317	2.704	0.508
90	1.732	2.021	0.633
120	1.162	1.356	0.753
150	0.809	0.944	0.828
180	0.556	0.649	0.882

$$k = 1.969 \times 10^{-4} \text{ sec}^{-1}$$

$$= 12.307 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 5

Feed: PBz + H_2S

Conditions: 330 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^2	Conversion X_{PBz}
0	--	4.600	0.000
15	3.477	4.059	0.118
30	3.079	3.591	0.219
60	2.293	2.675	0.418
90	1.555	1.815	0.605
120	1.242	1.449	0.685
150	1.038	1.211	0.737
180	0.553	0.645	0.860

$$k = 1.717 \times 10^{-4} \text{ sec}^{-1}$$

$$= 10.731 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 6

Feed: PBz + H_2S + NH_3

Conditions: 330 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	4.400	0.000
15	3.405	3.973	0.097
30	3.069	3.582	0.186
60	2.627	3.065	0.303
90	2.240	2.614	0.406
120	1.808	2.109	0.521
150	1.522	1.776	0.596
180	1.076	1.255	0.715

$$k = 1.089 \times 10^{-4} \text{ sec}^{-1}$$

$$= 6.811 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 6B

Feed: PBz + H_2S + NH_3

Conditions: 330 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	5.100	0.000
15	3.979	4.643	0.089
30	3.557	4.150	0.186
60	3.230	3.769	0.261
90	2.832	3.305	0.352
120	2.174	2.537	0.503
180	1.292	1.508	0.704

$$k = 1.076 \times 10^{-4} \text{ sec}^{-1}$$

$$= 6.725 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 7

Feed: PBz + H_2S + NH_3 + H_2O

Conditions: 330 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	4.500	0.000
15	3.432	4.005	0.111
35	3.244	3.786	0.159
60	2.882	3.363	0.253
90	2.253	2.629	0.416
120	2.167	2.529	0.438
180	0.959	1.120	0.701

$$k = 1.057 \times 10^{-4} \text{ sec}^{-1}$$

$$= 6.606 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 8

Feed: PBz only

Conditions: 350 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	5.500	0.000
15	3.694	4.311	0.216
30	2.863	3.341	0.393
50	2.509	2.929	0.467
80	1.600	1.867	0.661
120	1.031	1.203	0.781
165	0.489	0.570	0.896
180	0.337	0.393	0.929

$$k = 2.322 \times 10^{-4} \text{ sec}^{-1}$$

$$= 14.513 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 9

Feed: PBz + H_2S

Conditions: 350 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	5.500	0.000
15	3.913	4.566	0.170
30	3.473	4.052	0.263
50	2.574	3.003	0.454
70	2.159	2.519	0.542
90	1.778	2.075	0.623
120	1.115	1.301	0.763
150	0.771	0.899	0.837
180	0.481	0.561	0.898

$$k = 2.079 \times 10^{-4} \text{ sec}^{-1}$$

$$= 12.996 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 10

Feed: PBz + H_2S + NH_3

Conditions: 350 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	4.000	0.000
15	2.959	3.453	0.137
30	2.395	2.795	0.301
50	2.279	2.660	0.335
70	1.934	2.256	0.446
90	1.799	2.099	0.524
120	1.291	1.507	0.623

$$k = 1.329 \times 10^{-4} \text{ sec}^{-1}$$

$$= 8.306 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 11

Feed: PBz + H_2S + NH_3 + H_2O

Conditions: 350 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	3.600	0.000
15	2.723	3.177	0.125
35	2.497	2.913	0.212
50	1.884	2.199	0.493
70	1.566	1.828	0.678
90	1.381	1.621	0.803
120	1.210	1.412	0.936

$$k = 1.371 \times 10^{-4} \text{ sec}^{-1}$$

$$= 8.569 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 12

Feed: PBz only

Conditions: 375 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	5.500	0.000
10	4.207	4.610	0.164
30	3.052	3.562	0.352
50	2.131	2.487	0.548
70	1.662	1.939	0.647
100	0.927	1.082	0.803
130	0.616	0.616	0.888

$$k = 2.770 \times 10^{-4} \text{ sec}^{-1}$$

$$= 34.630 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 13

Feed: PBz + H_2S

Conditions: 375 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	5.150	0.000
10	3.827	4.466	0.133
30	2.727	3.182	0.382
50	2.363	2.757	0.465
70	1.703	1.987	0.614
100	1.017	1.187	0.769

$$k = 2.373 \times 10^{-4} \text{ sec}^{-1}$$

$$= 29.663 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 14

Feed: PBz + H_2S + NH_3

Conditions: 375 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	4.350	0.000
10	3.370	3.933	0.096
35	2.570	3.006	0.309
55	2.468	2.880	0.338
75	1.815	2.118	0.513
95	1.600	1.867	0.571
130	0.875	1.021	0.765

$$k = 1.761 \times 10^{-4} \text{ sec}^{-1}$$

$$= 22.013 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

Run # 15

Feed: PBz + H_2S + NH_3 + H_2O

Conditions: 375 °C, 1000 psig

Catalyst: Presulfided $NiMo/Al_2O_3$

Time (min)	Area Counts of PBz x 10^{-5}	Conc. of PBz gmol/lit x 10^{2}	Conversion X_{PBz}
0	--	4.100	0.000
10	2.999	3.500	0.125
35	2.059	2.403	0.399
55	2.002	2.336	0.436
75	1.804	2.105	0.524
90	1.307	1.526	0.619
120	0.969	1.126	0.728

$$k = 1.727 \times 10^{-4} \text{ sec}^{-1}$$

$$= 21.588 \times 10^{-6} \text{ m}^3/\text{kgcat.sec}$$

LITERATURE CITED

Aboul-Gheit, A. K., and I. K. Abdou, J. Instt. Petrol., 59 (568), 188 (1973).

Ahuja, S. P., M. L. Derrien and J. F. LePage, Ind. Engg. Chem.; Prod. Res. & Dev., 9 ,272 (1970).

Ali, M. F., A. Bukhari and M. Saleem, Ind. Engg. Chem.; Proc. Des. & Dev., 22 691 (1983).

de Beer, V. H. J., J. G. S. Dahlmans and J. G. M. Smeets, J. Catalysis, 42 457 (1976).

Bhinde, M. V., Ph.D dissertation, University of Delaware, Newark, Delaware, 1979.

Broderick, D. H. and B. C. Gates, Preprints ACS, Div. Fuel Chem., 25 ,(1), 53 (1980).

Broderick, D. H., A. V. Sapre, B. C. Gates, H. Kwart & G. C. A. Schuit, J. Catalysis, 73, 45 (1982).

Carberry, J. J., Chemical and Catalytic Reaction Engineering, McGraw-Hill, New York, 1976.

Chang, C. C. and A. J. Silvestri, Ind. Engg. Chem.; Proc. Des. & Dev., 13 313 (1974).

Chang, C. C. and A. J. Silvestri, Ind. Engg. Chem.; Proc. Des. & Dev., 15 161 (1976).

Cox, K. E., Ph.D. Thesis, Montana State College, Bozeman, Montana, 1972.

Desikan P., and C. H. Amberg, Can. J. Chem., 42 843 (1964)

Desikan, P. and C. H. Amberg, Can. J. Chem., 41 1966 (1963).

Doelman, J. and J. C. Vlugter, Proc. Sixth World Petrol. Congr., III, 247, Frankfurt, 1963.

Espino, R. L., J. E. Sobel, G. H. Singhal and G. A. Huff, Preprints ACS, Div. Pet. Chem., 23 (1), 46 (1978).

Flinn, R. A., O. A. Larson and H. Beuther, Hydro. Proc. & Petrol. Refin., 42 (9), 129 (1963).

Frye, C. G. and J. F. Mosby, Chem. Engg. Prog., 63, (9), 66 (1967).

Furimsky, E., Fuel, 57, 494 (1978).

Furimsky, E., AIChE Journal, 25, 306 (1979).

Furimsky, E., Ind. Engg. Chem.; Proc. Des. & Dev., 22 31 (1983).

Gates, B. C., J. R. Katzer, and G. C. A. Schuit, Chemistry of Catalytic Processes, Chapter 5, McGraw-Hill, New York, 1979.

Gates, B. C., J. R. Katzer, J. H. Olson, H. Kwart and A. B. Stiles, DOE reports, University of Delaware, Newark, Delaware, 1978.

Givens, E. N. and P.B. Venuto, Preprints ACS, Div. Pet. Chem., 15 (4), A183 (1970).

Gorbaty, M. L. and B. M. Harney (Eds.), Refining of Synthetic Crudes, Adv. Chem. Ser. No. 179, (1979).

Goudriaan, F., Ph.D. Dissertation, Twente Technical University, The Netherlands, 1974.

Gultekin, S., Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1980.

Gultekin, S., Chemica Acta Turcica, 9 (1), (1981).

Gultekin, S., S. A. Ali, and C. N. Satterfield, Ind. Engg. Chem.; Proc. Des. & Dev., 23 (1), 179 (1984).

Houalla, M., N. K. Nag, A. V. Sapre, D. H. Broderick and B. C. Gates, AIChE Journal, 24, 1015 (1978).

Houalla, M., D. H. Broderick, A. V. Sapre, N. K. Nag, V. H. deBeer, B. C. Gates and H. Kwart, J. Catalysis, 61, 523 (1980).

Hung, C. W., and J. Wei, Ind. Engg. Chem.; Proc. Des. & Dev., 19 250 (1977a).

Hung, C. W., and J. Wei, Ind. Engg. Chem.; Proc. Des. & Dev., 19 258 (1977b).

Katzer, J. R. and R. Sivasubramanian, Catal. Rev. Sci. Eng. 20 (2), 155 (1979).

Kilanowski, D. R. and B. C. Gates, J. Catalysis, 62, 70 (1980).

Krishnamurthy S., S. Panvelkar and Y. T. Shah, AIChE Journal, 27 (6) 994 (1981).

Lee, H. C., and J. B. Butt, J. Catalysis, 49 320 (1977).

Matar, S., SYNFUELS--Hydrocarbons of the Future, PennWell Publishing Co., Tulsa, Oklahoma, 1982.

Mayer, J. F., Sc.D. dissertation, Massachusetts Institute of Technology, Cambridge, Massachusetts, 1974.

McIlvried, H. G., Ind. Engg. Chem.; Proc. Des. & Dev., 10 (1), 125 (1971).

Mitchell, P. C. H., Catalysis, Vol. 1, p. 204, The Chemical

Society of London, 1977.

Nag, N. K., A. V. Sapre, D. H. Broderick and B. C. Gates, J. Catalysis, 57, 509 (1979).

Oleck, P. and Sherry Y., Ind. Engg. Chem.; Proc. Des. & Dev., 16 525 (1977).

Owens, P. J. and C. H. Amberg, Adv. Chem. Ser., 33 182 (1961).

Owens, P. J. and C. H. Amberg, Can. J. Chem., 40 941 (1962).

Patzer, J. F., R. J. Farrauto and A. A. Montagna, Ind. Engg. Chem.; Proc. Des. & Dev., 18 (4), 625 (1979).

Philliphson, J. J., paper presented at AIChE meeting, Houston, 1971.

Qader, S. A., and G. R. Hill, Ind. Engg. Chem.; Proc. Des. & Dev., 8 450 (1969).

Richardo, B. O., K. C. Pratt and T. L. Trimm, Fuel, 58, 309 (1979).

Reiff, E. K., M.ChE. Thesis, University of Delaware, Newark, Delaware, 1977.

Riley. K. L., Preprints ACS, Div. Pet. Chem., 1104 (1978).

Rollmann, L. D., J. Catalysis, 46 243 (1977)

Sapre, A. V., D. H. Broderick, D. Fraenkel, B. C. Gates and N. K. Nag, AIChE Journal, 1980.

Sapre, A. V. and B. C. Gates, Ind. Engg. Chem.; Proc. Des. & Dev., 21 (1), 86 (1982).

Sapre, A. V. and B. C. Gates, Ind. Engg. Chem.; Proc. Des. & Dev., 20 (1), 68 (1981).

Satterfield, C. N., Heterogeneous Catalysis in Practice, McGraw-Hill, New York, (1980).

Satterfield, C. N. and G. W. Roberts, AIChE Journal, 14, 159 (1968).

Satterfield, C. N., and J. F. Cocchetto, Ind. Engg. Chem.; Proc. Des. & Dev., 20 (1), 53 (1981).

Satterfield, C. N., and S. Gultekin, Ind. Engg. Chem.; Proc. Des. & Dev., 20 (1), 62 (1981).

Satterfield, C. N., and D. L. Carter, Ind. Engg. Chem.; Proc. Des. & Dev., 20 538 (1981).

Satterfield, C. N., and S. H. Yang, Ind. Engg. Chem.; Proc. Des. & Dev., 23 11 (1984).

Satterfield, C. N., and J. F. Cocchetto, AIChE Journal, 21, (6), 1107 (1975). Scheppele, T., Upgrading Coal Liquids, Adv. Chem. Ser. No. 156, (1981).

Schuit, G. C. A. and B. C. Gates, AIChE Journal, 19 417 (1973).

Schuman, S. C. and H. Shalit, Cat. Rev., 4 (2). 245 (1970).

Shih, S. S., J. R. Katzer, H. Kwart, and A. B. Stiles, Preprints ACS, Div. Pet. Chem., 22 919 (1977).

Smith, J. M., Chemical Engineering Kinetics, McGraw-Hill, New York, 1981.

Snyder, L. R., Preprints ACS, Div. Pet. Chem., 4 (2), C43 (1970).

Sonnemans, P., Ph.D. Thesis, Twente Technical University, The Netherlands, 1972.

Sonnemans, P. and T.Mars, J. Catalysis, 34 215 (1974).

Tamn, P. W., H. F. Harusberger and G. Bridge, Ind. Engg. Chem.; Proc. Des. & Dev., 20 262 (1978).

Voorhoeve, R. J. H., and J. C. M. Stuiver, J. Catalysis, 23 243 (1971).

Voorhoeve, R. J. H., and J. C. M. Stuiver, J. Catalysis, 23 228 (1971).

Weisser, O., and Landa, S., Sulfide Catalysts, Their Properties and Applications, Pergamannon Press, Oxford, New York, 1973.

Yang, S. H., and C. N. Satterfield, Ind. Engg. Chem.; Proc. Des. & Dev., 23 20 (1984).